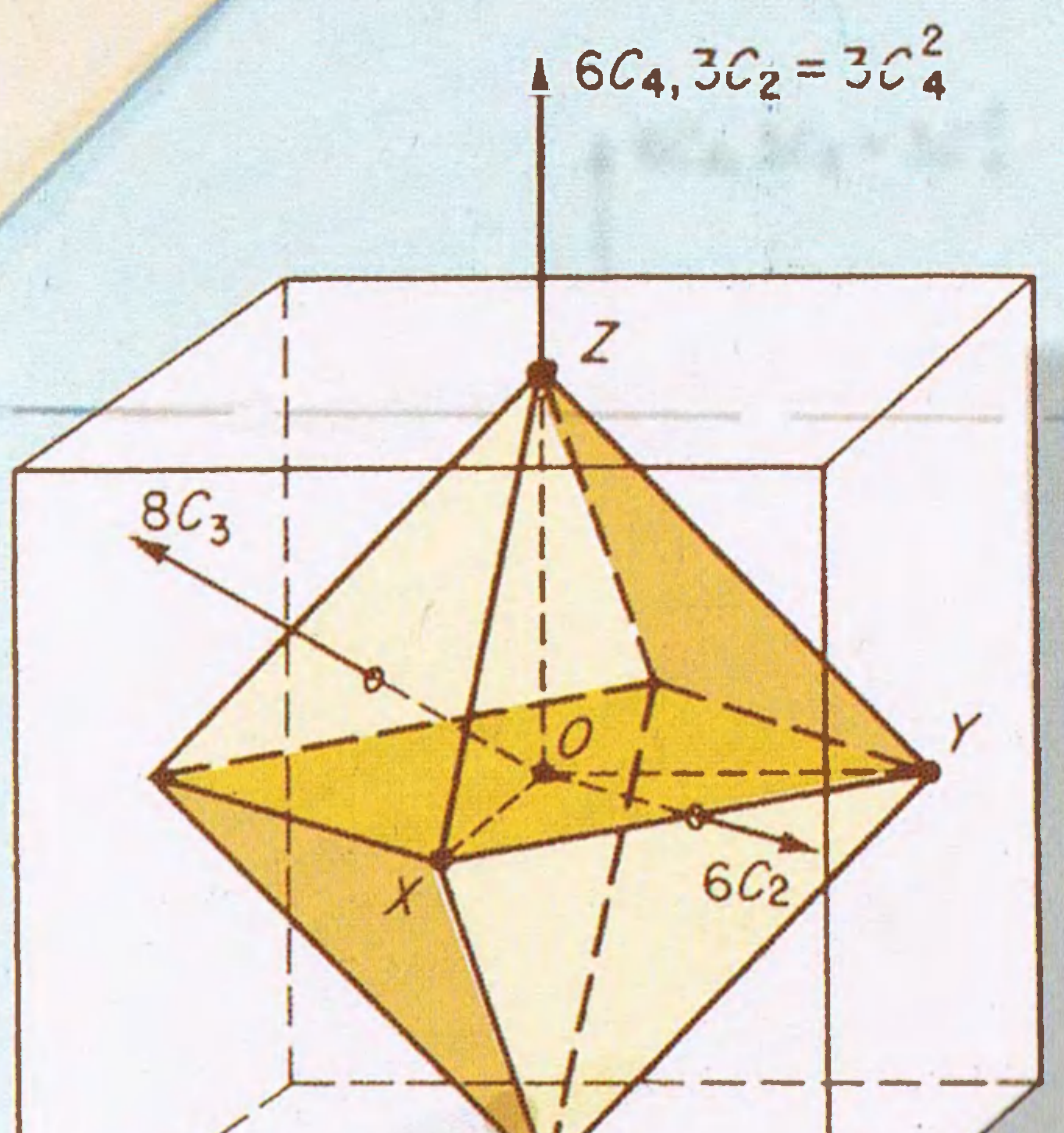
Group Theory and Quantum Mechanics

Michael Tinkham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GROUP THEORY
AND
QUANTUM MECHANICS

Michael Tinkham
Rumford Professor of Physics
and
Gordon McKay
Professor of Applied Physics
Harvard University

Reg. FC. 39230

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PREFACE

This book has developed from a set of mimeographed notes, written to accompany a series of 44 lectures which comprise a semester course on group theory and the quantum mechanics of atoms, molecules, and solids. The course has been given by the author to graduate students at the University of California since 1957. Since this course is followed by another dealing entirely with solid-state theory, the applications to solid-state problems in the book are largely limited to areas in which the apparatus of group theory is particularly essential. Because of the resulting emphasis on atomic and molecular problems, many chemists take the course, typically about a third of the class. Since students are assumed to have had a year of quantum theory as a prerequisite to the course, such standard elementary examples as the hydrogen atom and the harmonic oscillator have been dispensed with in the interest of brevity. However, a real attempt has been made throughout to keep the treatment as simple as possible and understandable to students with a variety of backgrounds. In particular, the group theory is developed on the assumption that the student has no previous knowledge of it, and elegant formal elaborations have been avoided in favor of presenting only a useful core of ideas as simply as possible. The treatment throughout is definitely intended to be useful to experimentalists who desire a better understanding of the current theoretical picture of the structure of atoms, molecules, and solids.

The book is intended for use as an introductory text rather than as a definitive treatise. Relatively little completely original work is presented. Rather, an attempt has been made to collect in a compact and unified form some of the scattered material on standard methods which is needed for an understanding of current research work.

The book divides logically into two parts. The first five chapters are primarily devoted to the introduction of methods, illustrated by physical examples, whereas the last three chapters present a systematic treatment of the quantum theory of atoms, molecules, and solids, additional methods being introduced as needed to handle specific problems as they arise.

After a brief introductory chapter, the formal theory of finite groups and their representation is developed in Chapters 2 and 3 in a manner which draws heavily on Wigner's classic "Group Theory." Chapter 4 is devoted to the illustration of the group theory. This is done by developing the crystallographic point groups which are basic for both solid-state and molecular theory. The classic work of Bethe on the splitting of atomic terms in crystalline fields of the various symmetries is then presented, including the introduction of the crystal double groups. This beautiful and illuminating work has not been readily accessible before, though basic for the theory of magnetic materials. As a final illustration of the point groups, we consider the directed-valence theory of hybrid orbitals.

Chapter 5 is devoted to the theory of systems with full rotational symmetry. First we develop the relation between angular momentum and transformation properties under rotation. Then, closely following Wigner, the homomorphism between the full rotation group and the unimodular unitary group is used to develop all the representations of the rotation group. From these, the Wigner or Clebsch-Gordan coefficients are derived in general form and applied through the Wigner-Eckart theorem to matrix elements of tensor operators. Finally, the Racah coefficients are introduced to handle more general problems arising in the application of tensor operators. This latter treatment is based on the monograph of Rose, "Elementary Theory of Angular Momentum." The chapter concludes with a discussion of space- and time-inversion symmetries and their consequences in parity conservation and Kramers' degeneracy.

The systematic presentation of atomic structure in Chapter 6 draws heavily on the monumental treatise by Condon and Shortley, "The Theory of Atomic Structure." In particular, the determinantal method developed by Slater is used for calculation of L-S-term energies and multiplet structure. However, the group-theoretical viewpoint is emphasized where it provides helpful insight, rather than being minimized. The Hartree-Fock method is treated, including Slater's modified form, and some reference is made to recent work on the unrestricted Hartree-Fock method. The rigorous group-theoretical derivation of the Landé g-factor formula is given, as is a discussion of the Paschen-Back transition in the Zeeman effect. The discussion of magnetic hyperfine structure follows that of Ramsey ("Nuclear Moments") but again makes more use of group-theoretical arguments. The electric hyperfine structure is treated as an application of the Racah coefficients, although the connection with the usual elementary approach is indicated.

Chapter 7 on molecular structure makes considerable use of material from "Quantum Chemistry" by Eyring, Walter, and Kimball. It opens with a discussion of the Born-Oppenheimer approximation. The rest of the chapter provides a systematic following through of the approximation. First the electronic energy levels for the problem of "clamped nuclei" are attacked, the method of molecular orbitals being emphasized. The group theory is employed in classifying and constructing these. With the electronic energy used as an effective potential, vibrational motion is discussed, together with the symmetry properties of combination and overtone levels in polyatomic molecules. The rotational energy of a rigid molecule is then considered, and a discussion of centrifugal distortion effects is given. At the end of the chapter a variety of cross terms which involve a higher-order Born-Oppenheimer approximation are indicated.

Chapter 8, on solid-state physics, treats two important topics of solid-state theory in which group-theoretical symmetry considerations are particularly useful, namely, electronic energy band theory and magnetic crystal symmetry. The general periodic-potential problem is set up, and some standard approximate approaches are discussed briefly, though the problems of actual quantitative calculations are not dealt with. The principal emphasis is on the group-theoretical discussion of the symmetry classification of wave functions in crystals, as initiated by Bouckaert, Smoluchowski, and Wigner and extended by many others. The introduction of spin-orbit coupling and the implications of time-reversal symmetry in band theory are indicated. This leads to a consideration of magnetic materials, in which time-reversal symmetry in the usual sense is not effective. The Shubnikov groups are developed, following Tavger and Zaitsev, and illustrated with examples. Finally, the Landau theory of second-order phase transitions is presented and applied to treat the change in symmetry of a magnetic material upon ordering.

As this summary indicates, a wide range of material, which introduces many techniques, is covered. An emphasis on the application of group theory to give insight into physical problems serves as a unifying principle. Of necessity, the treatment is rather brief, since with some few omissions the material is intended for a one-semester course. Accordingly, little material has been included merely for completeness. Rather, an attempt has been made to pick out some of the main features of the picture, things which should be part of the working understanding of nature for physicists and chemists. It is hoped that this approach will help the reader to acquire the new concepts and advanced methods and give him the sort of perspective which seems to be so easy to miss. He should then be able to continue with confidence to further independent study of particular topics required in his research work.

For the benefit of those who are familiar with the mimeographed version of this book, which has been widely circulated since 1957, we might note that the text has been completely rewritten in an effort to improve its clarity and completeness. New material added includes the entire final chapter on band theory and magnetic-crystal symmetry groups, a major expansion of the section on time-reversal symmetry, a major expansion of the treatment of molecular vibrations, a short discussion of the 3-*j* coefficients, a treatment of the Zeeman effect in atomic spectra, and problems at the end of each chapter. The new material, together with the general expansion of the old upon rewriting, accounts for the increase by about one-half in the length of the present volume compared with the notes.

The author wishes to acknowledge the contributions of Professors C. Kittel and R. Karplus, the notes from whose previous lecture courses provided the starting point for this book. Thanks are also due to many persons, particularly Professors L. I. Schiff, J. H. Van Vleck, and L. C. Allen, for their encouragement when the work was progressing slowly. The support of a John Simon Guggenheim Memorial Foundation grant and the hospitality of the Massachusetts Institute of Technology provided the author the opportunity to go over the proofs of the book with the care necessary to eliminate errors.

Finally, it is a pleasure to thank Dr. V. Heine for his very thorough and helpful scrutiny of the entire manuscript, which has eliminated many obscurities and some errors. The author is grateful for this help, and that of other reviewers of the manuscript, in improving the presentation, but he, of course, accepts all responsibility for the final result.

M. Tinkham

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1 INTRODUCTION

1-1 The Nature of the Problem

The basic task of quantum theory in the study of atoms, molecules, and solids consists in solving the time-independent Schrödinger equation

$$H\psi_n = E_n\psi_n$$

to determine the energy eigenvalues E_n and the corresponding eigenfunctions ψ_n. The reason for the preeminent position of energy eigenfunctions in the theory is, of course, that they form the stationary states of isolated systems in which energy must be conserved. The science of spectroscopy is devoted to discovering the eigenvalues E_n experimentally, so that one may work back to infer the internal structure of the system which produces them. Moreover, because of their simple time dependence ($e^{-iE_nt/\hbar}$), they can be used to build up a description of the time evolution of nonstationary systems as well. Thus a major share of the theoretical work in extranuclear physics is devoted to finding eigenstates and eigenvalues of the Hamiltonian operator.

Apart from spin and other relativistic effects, the Hamiltonian operator H is obtained from the classical expression for the energy $H(p_i, q_i)$ by making the usual operator replacement $\mathbf{p}_i \rightarrow (\hbar/i)\nabla_i$. Since we shall be dealing with low-energy phenomena, we may introduce the spin effects through the standard two-component Pauli matrix treatment, without resorting to the four-component Dirac equation. In other words, there is really no longer any serious difficulty in principle in writing down a basic Hamiltonian which is accurate enough for all practical purposes in extranuclear physics. (Within the nucleus, of course, the situation is quite different.) The difficulty is simply that the eigenvalue problems to be solved are very hard and complicated.

This is illustrated by writing down our Hamiltonian.

$$H = \sum_{\mathrm{el}} \frac{\mathbf{p}_j^{\,2}}{2m} + \sum_{\mathrm{nuc}} \frac{\mathbf{p}_K^{\,2}}{2M_K} - \sum_{\mathrm{nuc,el}} \frac{Z_K e^2}{r_{Kj}} + \sum_{\mathrm{nuc}} \frac{Z_K Z_L e^2}{r_{KL}} + \sum_{\mathrm{el}} \frac{e^2}{r_{ij}}$$

$$+ H_{so} + H_{ss} + H_{hfs} + H_{\mathrm{ext}}$$

where H_{so}, H_{ss}, H_{hfs}, and H_{ext} refer to spin-orbit, spin-spin, hyperfine-structure, and external-field couplings. The eigenfunctions of this operator will be functions of the space and spin coordinates of all the electrons and nuclei. Even for as simple a system as the oxygen molecule, O_2^{16}, this will involve a 54-dimensional spatial function together with 16 spin functions. It is clear that exact "textbook" solutions cannot be expected except for such simple cases as harmonic oscillators, single-particle central-field problems, and noninteracting particles in a square-walled box.

One might propose a direct brute-force numerical solution by use of high-speed digital computers. The impossibility of this approach may be seen by considering the difficulty of simply stating the wavefunction obtained, which is a $3N$-dimensional function (if there are N electrons and the nuclei are assumed fixed). For reasonable accuracy, we would need to divide each axis into, say, 100 units. Thus we would need to tabulate $(100)^{3N} = 10^{6N}$ entries. For something as simple as a four-electron system, this already exceeds the number of molecules in a mole, and our libraries could hardly contain the millions of volumes required to record the result. Needless to say, no human mind could comprehend a result hidden in such a mass of numbers. By making the sweeping, but reasonable, physical approximation of treating each particle as moving independently in an average field from the others, the problem can be reduced to large, but more manageable, dimensions. The detailed interactions could then be reintroduced as a correction, if a more refined calculation were required.

In any case, it is clear that the only practical approach to real physical problems, of any except the very simplest sort, will be an approximate one. The correct answer is approached by successively improved approximations, obtained by including successively smaller correction terms in the Hamiltonian and by increasing the accuracy with which any given approximation to the Schrödinger equation is satisfied. In many cases, this procedure can be carried far enough to yield a description adequate to explain all observed physical properties of the system under consideration, while remaining simple enough to be qualitatively helpful.

1-2 The Role of Symmetry

Being faced by the task of efficiently simplifying a problem so that it may be solved, it is clearly advantageous first to seek out any simplifications which can be made rigorously on the basis of symmetry. Only after these have been fully exploited should one resort to approximations which reduce the generality and accuracy of the final answer. To assist us in the search for the full symmetry-based simplification of the problem, we draw upon the resources of group theory. This provides us with a systematic calculus for exploiting symmetry properties to the fullest extent. Since we require only elementary group theory for our purposes, we shall be able to first develop this machinery from the very beginning. This involves a certain amount of "capital investment" in the form of learning some new formal methods. However, once this investment has been made, we are in a position to adduce very general results in many problems in an economical way, and to gain new insight. It seems inefficient to proceed in many quantum-mechanical problems without this tool at our disposal.

The symmetry which we aim to exploit via group theory is, in most cases, the symmetry of the Hamiltonian operator. To discuss this symmetry, it is convenient to introduce the concept of *transformation operators* which induce some particular coordinate transformation in whatever follows them. For example, the inversion operator i reverses the signs of all coordinates, taking $\mathbf{r}$ into $-\mathbf{r}$. Other common operators are those inducing reflections, rotations, translations, or permutations of coordinates of particles. Such an operator will be a *symmetry* operator appropriate to a given Hamiltonian if the Hamiltonian looks the same after the coordinate transformation as it did before; in other words, if the Hamiltonian is invariant under the transformation. For example, if the potential-energy expression is an even function of coordinates about the origin, it will be invariant under inversion. Since the kinetic-energy operator involves only second derivatives, it is always even. Hence the entire Hamiltonian is invariant under inversion if the potential is. This has useful consequences, as we shall soon see.

To continue this discussion, it is useful to note that if an operator R leaves the Hamiltonian invariant, $RH\psi = HR\psi$, for any ψ. That is to say, R will commute with H if it leaves H invariant. But if R commutes with H, a general theorem tells us that there are no matrix elements of H between eigenstates of R having different eigenvalues for the operator R. The proof is simple. Namely, in the equation

$$RH = HR$$

we may expand the products in a matrix representation based on eigenfunctions of R. Thus

$$\sum_j R_{ij}H_{jk} = \sum_j H_{ij}R_{jk}$$

But since the representation is based on eigenfunctions of R, R has a diagonal matrix and each sum reduces to a single term, namely,

$$R_{ii}H_{ik} = H_{ik}R_{kk}$$

or

$$(R_{ii} - R_{kk})H_{ik} = 0$$

Thus $H_{ik} = 0$ if i and k refer to different eigenvalues of R, as stated. The significance of this result to us is that, in searching for eigenfunctions that diagonalize the Hamiltonian operator, the search can be made separately within the classes of functions having different eigenvalues of a commuting symmetry operator since no off-diagonal matrix elements of H will connect functions of different symmetry. For example, considering inversion symmetry, we can find all possible energy eigenfunctions by considering only functions which are either even or odd under inversion. Roughly speaking, this cuts the detailed work in half, besides leading to some qualitative information about the solutions with practically no work at all.

If there are several mutually commuting symmetry operators, all of which commute with H, we can then choose basis functions which are simultaneous eigenfunctions of all these symmetry operators. It then follows that there are no matrix elements of H between states which differ in their classification according to any of the symmetry operators. Consequently, we must be able to find a complete set of eigenfunctions of H which are also eigenfunctions of our complete set of mutually commuting symmetry operators. Thus we may restrict our search for eigenfunctions of H to functions having a definite symmetry under this set of operators.

It is often the case that, after finding the largest group of mutually commuting symmetry operators, there may be additional symmetry operators which commute with the Hamiltonian but which do not commute with all the previous symmetry operators. Although this larger group of operators is not completely mutually commuting, some additional information can be obtained by using these symmetry operators. We shall show later that, although it is no longer possible to work with functions which are eigenfunctions of all the (larger group of) operators, finite sets of functions can be found such that the effect of a symmetry operation on one function of the set produces only a linear combination of functions within the set. These linear combinations are described by matrices which replace the simple eigenvalues described above as the entity describing the symmetry properties of the functions. The dimensionality of these matrices will turn out to give the degeneracy of the quantum-mechanical eigenfunctions, and the labels characterizing the various matrices and rows within the matrices will form the "good quantum numbers" for the system. These are the generalizations of the parity, or even versus oddness, "quantum number" in the simple example of inversion symmetry treated above. These matrices are the subject of the theory of group representations, which we shall consider in Chap. 3.

The results of group theory which we shall obtain are of considerable practical value, since the method of approximate solution almost invariably consists in expanding the solution in terms of a "suitable" set of approximate functions. Our group theoretical study of the symmetry of the system will enable us to choose zero-order functions of the correct symmetry so as to eliminate most off-diagonal matrix elements of H, leaving a largely simplified problem. Since we shall also see that symmetry determines selection rules, the selection rules governing transitions between these eigenfunctions can also be determined by group-theoretical arguments, without explicit integrations to compute matrix elements. Of course, there is also a quantitative calculation left to find the actual eigenfunctions, the eigenvalues, and the transition probabilities. However, the group theory will usually provide very considerable aid in reducing the scale of this residual calculation as well as giving some rigorous qualitative results with practically no effort at all.

We now proceed to develop the group-theoretical machinery before actually considering in detail the physical problems which are our primary concern.

2 ABSTRACT GROUP THEORY

2-1 Definitions and Nomenclature

By a group we mean a set of *elements* $A, B, C, \ldots$ such that a form of *group multiplication* may be defined which associates a third element with any ordered pair. This multiplication must satisfy the requirements:

1. The product of any two elements is in the set; i.e., the set is *closed* under group multiplication.

2. The *associative law* holds; for example, $A(BC) = (AB)C$.

3. There is a *unit element* E such that $EA = AE = A$.

4. There is in the group an inverse A^{-1} to each element A such that $AA^{-1} = A^{-1}A = E$.

For the present we shall restrict our attention primarily to *finite groups*. These contain a finite number h of group elements, where h is said to be the *order* of the group. If group multiplication is commutative, so that $AB = BA$ for all A and B, the group is said to be *Abelian.*

2-2 Illustrative Examples

An example of an Abelian group of infinite order is the set of all positive and negative integers including zero. In this case, ordinary addition serves as the group-multiplication operation, zero serves as the unit element, and $-n$ is the inverse of n. Clearly the set is closed, and the associative law is obeyed.

An example of a non-Abelian group of infinite order is the set of all $n \times n$ matrices with nonvanishing determinants. Here the group-multiplication operation is matrix multiplication, and the unit element is the $n \times n$ unit matrix. The inverse matrix of each matrix may be constructed by the usual methods,[1] since the matrices are required to have nonvanishing determinants.

A physically important example of a finite group is the set of covering operations of a symmetrical object. By a covering operation, we mean a rotation, reflection, or inversion which would bring the object into a form indistinguishable from the original one. For example, all rotations about the center are covering operations of a sphere. In such a group the product AB means the operation obtained by first performing B, then A. The unit operation is no operation at all, or perhaps a rotation through 2π. The inverse of each operation is physically apparent. For example, the inverse of a rotation is a rotation through the same angle in the reverse sense about the same axis.

As a complete example, which we shall often use for illustrative purposes, consider the non-Abelian group of order 6 specified by the following *group-multiplication table:*

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

The meaning of this table is that each entry is the product of the element labeling the row times the element labeling the column. For example, $AB = D \neq BA$. This table results, for example, if we take our elements to be the following six matrices, and if ordinary matrix multiplication is used as the group-multiplication operation:

---

[1] See Appendix A and references cited there.

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad A = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad B = \begin{pmatrix} \frac{-1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$$

$$C = \begin{pmatrix} \frac{-1}{2} & \frac{-\sqrt{3}}{2} \\ \frac{-\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} \qquad D = \begin{pmatrix} \frac{-1}{2} & \frac{\sqrt{3}}{2} \\ \frac{-\sqrt{3}}{2} & \frac{-1}{2} \end{pmatrix} \qquad F = \begin{pmatrix} \frac{-1}{2} & \frac{-\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{-1}{2} \end{pmatrix}$$

Verification of the table is left as a simple exercise.

The very same multiplication table could be obtained by considering the group elements $A, \ldots, F$ to represent the proper covering operations of an equilateral triangle as indicated in Fig. 2-1. The elements A, B, and C are rotations by π about the axes shown. Element D is a clockwise rotation by $2\pi/3$ in the plane of the triangle, and F is a counterclockwise rotation through the same angle. The numbering of the corners destroys the symmetry so that the position of the triangle can be followed through successive operations. If we make the convention that we consider the rotation axes to be kept fixed in space (not rotated with the object), it is easy to verify that the multiplication table given above describes this group as well.

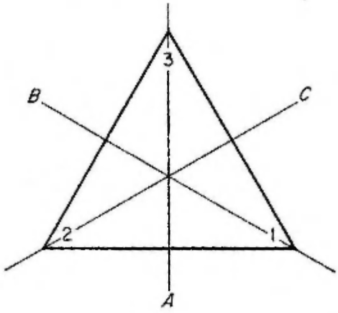

Fig. 2-1. *Symmetry axes of equilateral triangle.*

Two groups obeying the same multiplication table are said to be *isomorphic.*

2-3 Rearrangement Theorem

In the multiplication table in the example above, each column or row contains each element once and only once. This rule is true in general and is called the *rearrangement theorem.* Stated more formally, in the sequence

$$EA_k, A_2A_k, A_3A_k, \ldots, A_hA_k,$$

each group element A_i appears exactly once (in the form A_rA_k). The elements are merely rearranged by multiplying each by A_k.

PROOF: For any A_i and A_k, there exists an element $A_r = A_iA_k^{-1}$ in the group since the group contains inverses and is closed. Since $A_rA_k = A_i$ for this particular A_r, A_i must appear in the sequence at least once. But there are h elements in the group and h terms in the sequence. Hence there is no opportunity for any element to make more than a single appearance.

2-4 Cyclic Groups

For any group element X, one can form the sequence

$$X, X^2, X^3, \ldots, X^{n-1}, X^n = E$$

This is called the *period* of X, since the sequence would simply repeat this period over and over if it were extended. (Eventually we must find repetition, since the group is assumed to be finite.) The integer n is called the *order* of X, and this period clearly forms a group as it stands, although it need not exhaust all the elements of the group with which we started. Hence it may be said to form a *cyclic group* of order n. If it is indeed only part of a larger group, it is referred to as a cyclic *subgroup*.[1] We note that all cyclic groups must be Abelian.

In our standard example of the triangle, the period of D is D, $D^2 = F$, $D^3 = DF = E$. Thus D is of order 3, and D, F, E form a cyclic subgroup of our entire group of order 6.

2-5 Subgroups and Cosets

Let $\mathscr{S} = E, S_2, S_3, \ldots, S_g$ be a *subgroup* of order g of a larger group $\mathscr{G}$ of order h. We then call the set of g elements $EX, S_2X, S_3X, \ldots, S_gX$ a *right coset* $\mathscr{S}X$ if X is not in $\mathscr{S}$. (If X were in $\mathscr{S}$, $\mathscr{S}X$ would simply be the subgroup $\mathscr{S}$ itself, by the rearrangement theorem.) Similarly, we define the set $X\mathscr{S}$ as being a *left coset.* These cosets cannot be subgroups, since they cannot include the identity element. In fact, a coset $\mathscr{S}X$ contains *no* elements in common with the subgroup $\mathscr{S}$.

The proof of this statement is easily given by assuming, on the contrary, that for some element S_k we have $S_kX = S_l$, a member of $\mathscr{S}$. Then $X = S_k^{-1}S_l$, which is in the subgroup, and $\mathscr{S}X$ is not a coset at all, but just $\mathscr{S}$ itself.

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[1] Although the concept is introduced here in connection with cyclic groups, subgroups need not be cyclic. Any subset of elements within a group which in itself forms a group is called a subgroup of the larger group.

Next we note that two right (or left) cosets of subgroup $\mathscr{S}$ in $\mathscr{G}$ either are identical or have no elements in common.

PROOF: Consider two cosets $\mathscr{S}X$ and $\mathscr{S}Y$. Assume that there exists a common element $S_kX = S_lY$. Then $XY^{-1} = S_k^{-1}S_l$, which is in $\mathscr{S}$. Therefore $\mathscr{S}XY^{-1} = \mathscr{S}$. by the rearrangement theorem. Postmultiplying both sides by Y leads to $\mathscr{S}X = \mathscr{S}Y$. Thus the two cosets are completely identical if a single common element exists.

If we combine the results of the preceding paragraphs, we can prove the following theorem: *The order g of a subgroup must be an integral divisor of the order h of the entire group.* That is, $h/g = l$, where the integer l is called the *index* of the subgroup $\mathscr{S}$ in $\mathscr{G}$.

PROOF: Each of the h elements of $\mathscr{G}$ must appear either in $\mathscr{S}$ or in a coset $\mathscr{S}X$, for some X. Thus each element must appear in one of the sets $\mathscr{S}, \mathscr{S}X_2, \mathscr{S}X_3, \ldots, \mathscr{S}X_l$, where we have listed all the *distinct* cosets of $\mathscr{S}$ together with $\mathscr{S}$ itself. But we have shown that there are no elements common to any of these collections of g elements. Hence it must be possible to divide the total number of elements h into an integral number of sets of g each, and consequently $h = l \times g$.

As an example, consider the subgroup $\mathscr{S} = A, E$ of our illustrative group of order 6. The right cosets with B and D are identical, namely, $\mathscr{S}B = \mathscr{S}D = B, D$. Also $\mathscr{S}C = \mathscr{S}F = C, F$. We note that, as proved in general, these cosets contain no common elements unless entirely identical and they contain no elements in common with $\mathscr{S}$. Also, the order (2) of the subgroup *is* an integral divisor of the order (6) of the group. To generalize, the order of *any* cyclic subgroup formed by the period of some group element must be a divisor of the order of the group.

2-6 Example Groups of Finite Order

1. *Groups of order* 1. The only example is the group consisting solely of the identity element E.

2. *Groups of order* 2. Again there is only one possibility, the group $(A, A^2 = E)$. This is an Abelian group, and in physical applications A might represent reflection, inversion, or an interchange of two identical particles.

3. *Groups of order* 3. In this case, if we start with two elements A and E, it must be that $A^2 = B \neq E$. Otherwise, if A^2 were to equal E, then (A, E) would form a subgroup of order 2 in a group of order 3, which would violate our theorem. Thus the only possibility is the cyclic group $(A, A^2 = B, A^3 = E)$.

4. *Groups of order* 4. With order 4 we begin to have more than one possible distinct group-multiplication table of given order. The two possibilities here are (1) the cyclic group $(A, A^2, A^3, A^4 = E)$ and (2) the so-called *Vierergruppe* (A, B, C, E) whose multiplication table is:

	E	A	B	C
E	E	A	B	C
A	A	E	C	B
B	B	C	E	A
C	C	B	A	E

Both these groups are Abelian, and in both cases we can pick out subgroups of order 2, as allowed by our theorem. A physical example of the cyclic group of order 4 is provided by the four fold rotations about an axis. On the other hand, the *Vierergruppe* is the rotational-symmetry group of a rectangular solid, if A, B, C are taken to be the rotations by π about the three orthogonal symmetry axes.

5. *Groups of prime order.* These must all be cyclic Abelian groups. Otherwise the period of some element would have to appear as a subgroup whose order was a divisor of a prime number. This general result allows us to note at once that there can be only single groups of order 1, 2, 3, 5, 7, 11, 13, etc.

6. *Permutation groups (of factorial order).* One group of order $n!$ can always be set up based on all the permutations of n distinguishable things. (Of course, others, such as a cyclic group, can also be found.) A permutation can be specified by a symbol such as

$$\begin{pmatrix} 1 & 2 & 3 & \cdots & n \\ \alpha_1 & \alpha_2 & \alpha_3 & \cdots & \alpha_n \end{pmatrix}$$

where $\alpha_1, \alpha_2, \ldots, \alpha_n = 1, 2, \ldots, n$, except for order. The permutation described by this symbol is one in which the item in position i is shifted to the position indicated in the lower line. Successive permutations form the group-multiplication operation. As an example, our standard example group of order 6 can be viewed as the permutation group of the three numbered corners of the triangle. The permutations may be expressed in the above notation as

$$E = \begin{pmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \end{pmatrix} \qquad A = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix} \qquad B = \begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix}$$

$$C = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix} \qquad D = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix} \qquad F = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix}$$

For example, operator A interchanges corners 1 and 2, whereas D replaces 1 by 3, 2 by 1, and 3 by 2, corresponding to a clockwise rotation by $2\pi/3$.

Applying B followed by A leads to

$$AB = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix}\begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix} = D$$

which is consistent with the group-multiplication table worked out previously.

Because of the identity of like particles, permutation of them leaves the Hamiltonian invariant. Accordingly, the permutation group plays an important role in quantum theory.

2-7 Conjugate Elements and Class Structure

An element B is said to be *conjugate* to A if

$$B = XAX^{-1} \qquad \text{or} \qquad A = X^{-1}BX$$

where X is some member of the group. Clearly this is a reciprocal property of the pair of elements. Further, if B and C are both conjugate to A, they are conjugate to each other.

PROOF: Assume that

$$B = XAX^{-1} \qquad \text{and} \qquad C = YAY^{-1}$$

Then $$A = Y^{-1}CY$$

and $$B = XY^{-1}CYX^{-1} = (XY^{-1})C(XY^{-1})^{-1}$$
$$= ZCZ^{-1}$$

[In this proof we have used the fact that the inverse of the product of two group elements is the product of the inverses of the elements in inverse order. This is clearly true, since $(RS)(S^{-1}R^{-1}) = R(SS^{-1})R^{-1} = RR^{-1} = E$.]

The properties of conjugate elements given above allow us to collect all mutually conjugate elements into what is called a *class* of elements. The class including A_i is found by forming all products of the form

$$EA_iE^{-1} = A_i, \; A_2A_iA_2^{-1}, \ldots, A_hA_iA_h^{-1}$$

Of course, some elements may be found several times by this procedure. By proceeding in this way, we can divide all the elements of the group among the various distinct classes. Luckily, we may usually avoid this rather tedious method by using physical-symmetry considerations, as shown below. For example, in the group of covering operations of an equilateral triangle, the two rotations by $2\pi/3$ form a class, the three rotations by π form a class, and, as always, *the identity element is in a class by itself.* The latter follows, since $AEA^{-1} = AA^{-1} = E$ for all A. Note that E is the *only class* which is also a *subgroup,* since all other classes must lack the identity element.

In Abelian groups, each element is in a class by itself, since $XAX^{-1} = AXX^{-1} = AE = A$.

If the group elements are represented by matrices, the traces of all elements in a class must be the same. This follows, since in this case the operation of conjugation becomes that of making a similarity transformation, which leaves the trace invariant.[1]

Physical interpretation of class structure. In physical applications the group elements can often be considered to be symmetry operations which are the covering operations of a symmetrical object. In this case, the operation $B = X^{-1}AX$ is the net operation obtained by first rotating the object to some equivalent position by X, next carrying out the operation A, and then undoing the initial rotation by X^{-1}. Thus B must be an operation of the same physical sort as A, such as a rotation through the same angle, but performed about some different (but physically equivalent) axis which is related to the axis of A by the group operation X^{-1}. This is the significance of operators being in the same class.

As a concrete example, consider the covering operations of the equilateral triangle indicated in Fig. 2-1. If we consider the conjugation of A with D, we have $D^{-1}AD = C$. To follow this through in detail, D rotates the triangle clockwise by $2\pi/3$ so that vertex 2 instead of 3 lies on axis A; next the rotation by π about the A axis interchanges 1 and 3; finally $D^{-1} = F$ rotates the triangle back $2\pi/3$ counterclockwise. This sequence leaves precisely the result of a single rotation by π about axis C, which is an axis equivalent to A but rotated $2\pi/3$ counterclockwise by the symmetry operator D^{-1}.

2-8 Normal Divisors and Factor Groups

If a subgroup $\mathscr{S}$ of a larger group $\mathscr{G}$ consists entirely of complete classes, it is called an *invariant subgroup*, or *normal divisor*. By consisting of complete classes, we mean that, if an element A is in $\mathscr{S}$, then all elements $X^{-1}AX$ are in $\mathscr{S}$, even when X runs over elements of $\mathscr{G}$ which are not in $\mathscr{S}$. Such a subgroup is called invariant because by the rearrangement theorem it is unchanged (except for order) by conjugation with any element of $\mathscr{G}$.

To allow a compact discussion, we introduce the notion of a *complex* such as $\mathscr{K} = (K_1, K_2, \ldots, K_n)$, which is a collection of group elements disregarding order. Such a complex can be multiplied by a single element or by another complex. For example,

$$\mathscr{K}X = (K_1X, K_2X, \ldots, K_nX)$$

and

$$\mathscr{K}\mathscr{R} = (K_1R_1, K_1R_2, \ldots, K_1R_m, \ldots, K_nR_m)$$

---

[1] See Appendix A.

Elements are considered to be included only once, regardless of how often they are generated.

We can now state our argument concisely by treating sets of elements as complexes. First, a subgroup is defined by the property of closure, that is, $\mathcal{S}\mathcal{S} = \mathcal{S}$. Second, if $\mathcal{S}$ is an *invariant* subgroup, then $X^{-1}\mathcal{S}X = \mathcal{S}$, for all X in the group $\mathcal{G}$. From this it follows that $\mathcal{S}X = X\mathcal{S}$, or, in words, the left and right cosets of an invariant subgroup are identical.

In Sec. 2-5 we have shown that there are a finite number $(l - 1)$ of distinct cosets for any subgroup $\mathcal{S}$. We may denote each of these as a complex, and if $\mathcal{S}$ is an invariant subgroup, we have, for example, $\mathcal{K}_i = \mathcal{S}K_i = K_i\mathcal{S}$. Note that $\mathcal{S}K_i = \mathcal{S}K_j$ if K_i and K_j are group elements in the same coset, since we are not concerned with the order in which the elements of the complex appear. Together with the subgroup $\mathcal{S}$, this set of $(l - 1)$ distinct complexes can themselves be regarded as the elements of a smaller group (of order $l = h/g$) on a higher level of abstraction. This new group is called the *factor group* of $\mathcal{G}$ with respect to the *normal divisor* (or invariant subgroup) $\mathcal{S}$. In this factor group, $\mathcal{S}$ forms the unit element. We can see this by considering

$$\mathcal{S}\mathcal{K}_i = \mathcal{S}(\mathcal{S}K_i) = (\mathcal{S}\mathcal{S})K_i = \mathcal{S}K_i = \mathcal{K}_i$$

Group multiplication works out as shown in the following example,

$$\mathcal{K}_i\mathcal{K}_j = (\mathcal{S}K_i)(\mathcal{S}K_j) = K_i\mathcal{S}\mathcal{S}K_j = K_i\mathcal{S}K_j = \mathcal{S}(K_iK_j) = (\mathcal{K}_i\mathcal{K}_j)$$

where the last expression refers to the complex which is the coset associated with the product K_iK_j. The concept of factor groups and normal divisors will prove useful in analyzing the structure of groups.

Isomorphy and homomorphy. We have already introduced the concept of isomorphy by noting that two groups having the same multiplication table are called isomorphic. This means that there is a one-to-one correspondence between the elements $A, B, \ldots$ of one group and those $A', B', \ldots$ of the other, such that $AB = C$ implies $A'B' = C'$, and vice versa.

Two groups are said to be *homomorphic* if there exists a correspondence between the elements of the two groups of the sort $A \leftrightarrow A_1', A_2', \ldots$. By this we mean that, if $AB = C$, then the product of any A_i' with any B_j' will be a member of the set C_k'. In general, a homomorphism is a many-to-one correspondence, as indicated here. It specializes to an isomorphism if the correspondence is one-to-one. For example, the group containing the single element E is homomorphic to any other group, since, in view of the fact that each group element is represented by E, group multiplication reduces simply to $EE = E$. A much less trivial example is provided by the homomorphic relation between any group and one of its factor groups (if it has one). The invariant subgroup $\mathcal{S}$ corresponds to all the members of $\mathcal{S}$, and the cosets $\mathscr{K}_i = \mathscr{S}K_i$ correspond to all members of the coset (including K_i and all other group elements having the same coset, which are just the members of $\mathscr{K}_i$). Thus, if $\mathscr{S}$ is of order g, there is a g-to-one correspondence between the original group elements and the elements of the factor group.

2-9 Class Multiplication

In this section we consider a different form of multiplication of collections of group elements in which we do keep track of the number of times an element appears. That is, $\mathscr{R} = \mathscr{K}$ implies that each element appears as often in $\mathscr{R}$ as in $\mathscr{K}$. In this notation

$$X^{-1}\mathscr{C}X = \mathscr{C} \tag{2-1}$$

where $\mathscr{C}$ is any complete *class* of the group and X is any element of the group. (PROOF: Each element produced on the left must appear on the right because they are all conjugate to elements in $\mathscr{C}$ and hence are in $\mathscr{C}$ by the definition of a class. But each element on the left is different, because of the uniqueness of group multiplication, as is each on the right. These two statements are consistent only if the two sides of the equation are equal.)

The converse of this theorem is also true: any collection $\mathscr{C}$ obeying (2-1) for all X in the group is comprised wholly of complete classes. (PROOF: First subtract all complete classes from both sides and denote any remainder by $\mathscr{R}$. Now consider any element R_i of $\mathscr{R}$ on the left in $X^{-1}\mathscr{R}X = \mathscr{R}$. Since this is assumed true for all X, $\mathscr{R}$ must by definition include the complete class of R. Thus $\mathscr{C}$ must be composed of complete classes.)

If we now apply the theorem (2-1) to the product of two classes, we have

$$\begin{aligned} \mathscr{C}_i\mathscr{C}_j &= X^{-1}\mathscr{C}_iXX^{-1}\mathscr{C}_jX \\ &= X^{-1}(\mathscr{C}_i\mathscr{C}_j)X \end{aligned}$$

for all X. Then, upon applying the converse theorem, it follows that $\mathscr{C}_i\mathscr{C}_j$ consists of complete classes. This may be expressed formally by writing

$$\mathscr{C}_i\mathscr{C}_j = \sum_k c_{ijk}\mathscr{C}_k \tag{2-2}$$

where c_{ijk} is the integer telling how often the complete class $\mathscr{C}_k$ appears in the product $\mathscr{C}_i\mathscr{C}_j$.

As an example, in the symmetry group of the triangle whose class structure we noted earlier, let $\mathscr{C}_i = E$; $\mathscr{C}_2 = A, B, C$; and $\mathscr{C}$ Then $\mathscr{C}_1\mathscr{C}_2 = \mathscr{C}_2$; $\mathscr{C}_1\mathscr{C}_3 = \mathscr{C}_3$; $\mathscr{C}_2\mathscr{C}_2 = 3\mathscr{C}_1 + 3\mathscr{C}_3$; $\mathscr{C}_2\mathscr{C}_3 = 2\mathscr{C}$

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EXERCISES

2-1 Consider the symmetry group of the proper covering operations of a square (D_4). This consists of eight elements:

E = the identity

A, B, C, D = 180° rotations about the corresponding labeled axes in Fig. 2-2 which are considered fixed in *space*, not on the body

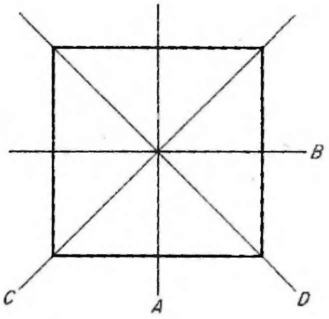

Fig. 2-2. *Symmetry axes of square.*

F, G, H = clockwise rotations in plane of the paper by $\pi/2$, π, and $3\pi/2$, respectively

(*a*) From the geometry, work out the multiplication table of the group; take advantage of the rearrangement theorem to check your result.

(*b*) From the nature of the operations, divide the group elements into classes. If in doubt, check by using the multiplication table [from (*a*)] and the definition of conjugate elements.

(*c*) Write down all the subgroups of the complete group. Note that the orders of the subgroups must be divisors of 8. Which of these subgroups are invariant subgroups (normal divisors)?

(*d*) Work out the cosets of the normal divisors.

(*e*) Work out the group-multiplication tables of the factor groups corresponding to the nontrivial normal divisors of the group.

(*f*) Determine the coefficients c_{ijk} appearing in all class multiplication products.

2-2 List the symmetries of a general rectangle. Work out the multiplication table, and divide the elements into classes.

2-3 Use the multiplication table for the symmetry group of the triangle to verify in several cases the rule for the inverse of a product.

2-4 Consider the group of order $(p - 1)$ obtained by taking as group elements the integers $1, 2, \ldots, (p - 1)$ and as group multiplication ordinary multiplication modulo p, where p is a prime number. (Modulo p means that $m + np$ is considered to be equal to m, where m and n are any integers.)

(*a*) Show that this is a group, and work out the multiplication table when $p = 7$.

(*b*) Prove in general that $A^{p-1} = E$, for all elements A of the group. In this way you have proved Fermat's number-theoretical theorem that $n^p = n(\mathrm{mod}\, p)$, where n is an integer and p is a prime.

(*c*) Check the theorem for $p = 7$ and $n = 2, 3, 5$.

2-5 Prove that all elements in the same class have the same order when used to generate a cyclic group.

2-6 Show that there is a homomorphism between the cyclic groups of order 4 and 2.

2-7 Prove that a group is Abelian if, and only if, the correspondence of each element to its inverse forms an isomorphism.

2-8 Prove that $c_{ijk} = c_{jik}$ in Eq. (2-2). In other words, prove that $\mathscr{C}_i\mathscr{C}_j = \mathscr{C}_j\mathscr{C}_i$, even if the group is not Abelian.

REFERENCES

BIRKHOFF, G., and S. MACLANE: "A Survey of Modern Algebra," chap. 6, The Macmillan Company, New York, 1949.

LEDERMANN, W.: "Introduction to the Theory of Finite Groups," 2d ed., Oliver & Boyd Ltd., Edinburgh and London, 1953.

SPEISER, A.: "Die Theorie der Gruppen von endlicher Ordnung," 3d ed., Springer-Verlag OHG, Berlin, 1937; reprinted by Dover Publications, Inc., New York, 1945.

WIGNER, E. P.: "Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra," chaps. 7 and 8, Academic Press Inc., New York, 1959.

3 THEORY OF GROUP REPRESENTATIONS

3-1 Definitions

By a *representation* of an abstract group we mean in general any group composed of concrete mathematical entities which is homomorphic to the original group. However, we shall restrict our attention to representation by square matrices, with matrix multiplication as the group multiplication operation. That is, we associate a matrix $\mathbf{\Gamma}(A)$ with each group element A in such a way that

$$\mathbf{\Gamma}(A)\mathbf{\Gamma}(B) = \mathbf{\Gamma}(AB)$$

These matrices then satisfy the group-multiplication table and in every way "represent" the abstract group elements. Clearly this is possible only if $\mathbf{\Gamma}(E) = \mathbf{E}$, the unit matrix. The number of rows and columns in the matrix is called the *dimensionality* of the representation.

If each matrix is different, then the two groups are isomorphic rather than merely homomorphic and the representation is said to be *true*, or *faithful*. On the other hand, if several elements correspond to a single matrix, one can easily see that all elements corresponding to the unit matrix form an invariant subgroup of the full group. Similarly, the elements corresponding to each of the other matrices of the representation form the distinct cosets of the invariant subgroup, and the matrices form a true representation of the factor group of this invariant subgroup.

Obviously the 2 × 2 matrices introduced in Sec. 2-2 form a true matrix representation of our standard example group of order 6. Another representation of the same group can be obtained by taking the determinant of each matrix, because of the fact that

$$|\mathbf{\Gamma}(A)| \cdot |\mathbf{\Gamma}(B)| = |\mathbf{\Gamma}(A)\mathbf{\Gamma}(B)| = |\mathbf{\Gamma}(AB)|$$

This operation reduces the matrices to ordinary numbers, namely, ± 1, giving a one-dimensional representation. This representation is no longer true, since there are only two distinct "matrices," whereas there are six group elements. A still simpler one-dimensional representation is obtained by representing each element by $+1$. This corresponds to the rather trivial homomorphism which can be set up by associating the unit element with all members of the original group, and it is often called the *identical representation.* We shall soon be able to prove that these three form the only possible, essentially different representations of the example group. After we establish the close connection between these matrix representations and quantum-mechanical eigenfunctions, it will become clear that such unconditional statements of group theory will have great practical value.

In discussing the various possible matrix representations of a group, it is important to note that a similarity transformation leaves matrix equations unchanged. That is, if we define $\mathbf{\Gamma}'(A) = \mathbf{S}^{-1}\mathbf{\Gamma}(A)\mathbf{S}$, then

$$\begin{aligned}\mathbf{\Gamma}'(A)\mathbf{\Gamma}'(B) &= [\mathbf{S}^{-1}\mathbf{\Gamma}(A)\mathbf{S}][\mathbf{S}^{-1}\mathbf{\Gamma}(B)\mathbf{S}] = \mathbf{S}^{-1}\mathbf{\Gamma}(A)\mathbf{\Gamma}(B)\mathbf{S}\\ &= \mathbf{S}^{-1}\mathbf{\Gamma}(AB)\mathbf{S} = \mathbf{\Gamma}'(AB)\end{aligned}$$

and the transformed matrices $\mathbf{\Gamma}'$ form a representation if the $\mathbf{\Gamma}$ matrices do. However, the infinity of representations related to each other in this way for various matrices $\mathbf{S}$ differ only in that they are stated with respect to different coordinate axes of some sort, and hence all are considered to be *equivalent.*

Reducible and irreducible representations. Clearly one can take two (or more) representations and construct from them a new representation by combining the matrices into larger matrices. For a typical element, we could form

$$\mathbf{\Gamma}(A) = \begin{pmatrix} \mathbf{\Gamma}^{(1)}(A) & \mathbf{0} \\ \mathbf{0} & \mathbf{\Gamma}^{(2)}(A) \end{pmatrix}$$

where $\mathbf{\Gamma}^{(1)}(A)$ and $\mathbf{\Gamma}^{(2)}(A)$ are the matrices representing element A in the original representations and $\mathbf{\Gamma}(A)$ represents A in the new larger representation. However, such an artificially enlarged matrix representation is said to be *reducible*. This reducibility might be concealed by applying a similarity transformation which scrambles rows and columns, leaving an equivalent representation which is *not* in block form. Thus our real criterion for reducibility is that it be possible to reduce the matrices representing *all* the elements of the group to block form (with the same block structure) by the *same* similarity transformation. If this *cannot* be done, a representation is said to be *irreducible*, meaning that it cannot be expressed in terms of representations of lower dimensionality. It is customary to indicate the structure of reducible representations by giving the irreducible representations which form the blocks after reduction to block form. In our example, we would write $\Gamma = \Gamma^{(1)} + \Gamma^{(2)}$; more generally, $\Gamma = \Sigma\, a_i \Gamma^{(i)}$, where the a_i are integers telling how often $\Gamma^{(i)}$ appears in Γ. (Observe that this notation does *not* refer to matrix addition.) In many quantum-mechanical applications each irreducible representation will display the transformation properties of a set of degenerate eigenfunctions. Hence, as we shall see, the number of irreducible representations may give the number of distinct energy levels, a very useful piece of information.

3-2 Proof of the Orthogonality Theorem

We commence this section by proving several lemmas leading up to the orthogonality theorem which is central to the development of the theory of group representations. The method of proof given here follows closely that in Wigner's classic book.[1] A review of the various properties of matrices which are used here may be found in Appendix A.

LEMMA: Any representation by matrices with nonvanishing determinants is equivalent through a similarity transformation to a representation by *unitary* matrices.

PROOF: For simplicity in notation let the matrix representing the element A_i be written $\mathbf{A}_i$. We can then construct a Hermitian matrix $\mathbf{H}$ by

$$\mathbf{H} = \sum_{i=1}^{h} \mathbf{A}_i \mathbf{A}_i^{\dagger} \tag{3-1}$$

since each term is already Hermitian. (In our notation a matrix is Hermitian if $\mathbf{H}^{\dagger} = \mathbf{H}$, or $H_{ji}^{*} = H_{ij}$.) But it is well known[2] that any Hermitian matrix can be diagonalized by the unitary transformation made up from the orthonormal eigenvectors found by solving the associated secular equation. Thus we can write

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[1] E. P. Wigner, "Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren," Friedr. Vieweg & Sohn, Brunswick, Germany, 1931; revised and translated edition, Academic Press Inc., New York, 1959.

[2] See Appendix A.

$$\begin{aligned}\mathbf{d} &= \mathbf{U}^{-1}\mathbf{H}\mathbf{U} = \sum_i \mathbf{U}^{-1}\mathbf{A}_i\mathbf{A}_i{}^{\dagger}\mathbf{U} \\ &= \sum_i \mathbf{U}^{-1}\mathbf{A}_i\mathbf{U}\mathbf{U}^{-1}\mathbf{A}_i{}^{\dagger}\mathbf{U} = \sum_i \mathbf{A}_i'\mathbf{A}_i'^{\dagger}\end{aligned} \tag{3-2}$$

where the primed matrices differ from the original ones by the unitary transformation **U**. Consideration of a typical element shows that not only is **d** diagonal but it has only real positive diagonal elements. This enables us to form other real positive diagonal matrices for $\mathbf{d}^{\frac{1}{2}}$ and $\mathbf{d}^{-\frac{1}{2}}$ by simply taking the appropriate power of the elements of **d**. Taking advantage of the commutation of diagonal matrices, we can then write (3-2) as

$$\mathbf{E} = \mathbf{d}^{-\frac{1}{2}} \sum_i \mathbf{A}_i'\mathbf{A}_i'^{\dagger}\, \mathbf{d}^{-\frac{1}{2}}$$

where **E** is the unit matrix. We can also define a new set of doubly transformed matrices by $\mathbf{A}_j'' = \mathbf{d}^{-\frac{1}{2}}\mathbf{A}_j'\mathbf{d}^{\frac{1}{2}}$. We conclude the proof by showing that these matrices $\mathbf{A}_j''$ are unitary.

To do this, consider

$$\begin{aligned}\mathbf{A}_j''\mathbf{A}_j''^{\dagger} &= \mathbf{d}^{-\frac{1}{2}}\mathbf{A}_j'\mathbf{d}^{\frac{1}{2}}[\mathbf{d}^{-\frac{1}{2}}\sum_i \mathbf{A}_i'\mathbf{A}_i'^{\dagger}\mathbf{d}^{-\frac{1}{2}}]\mathbf{d}^{\frac{1}{2}}\mathbf{A}_j'^{\dagger}\mathbf{d}^{-\frac{1}{2}} \\ &= \mathbf{d}^{-\frac{1}{2}}\sum_i \mathbf{A}_j'\mathbf{A}_i'\mathbf{A}_i'^{\dagger}\mathbf{A}_j'^{\dagger}\mathbf{d}^{-\frac{1}{2}} \\ &= \mathbf{d}^{-\frac{1}{2}}\sum_i \mathbf{A}_j'\mathbf{A}_i'(\mathbf{A}_j'\mathbf{A}_i')^{\dagger}\mathbf{d}^{-\frac{1}{2}} \\ &= \mathbf{d}^{-\frac{1}{2}}\sum_k \mathbf{A}_k'\mathbf{A}_k'^{\dagger}\mathbf{d}^{-\frac{1}{2}} = \mathbf{E}\end{aligned}$$

In making the change to the sum on k we have used the rearrangement theorem. Since we have shown that $\mathbf{A}_j''\mathbf{A}_j''^{\dagger} = \mathbf{E}$, we have shown that $\mathbf{A}_j''$ is unitary. Hence we can always construct a unitary representation from any given one by forming

$$\mathbf{A}_j'' = \mathbf{d}^{-\frac{1}{2}}\mathbf{U}^{-1}\mathbf{A}_j\mathbf{U}\mathbf{d}^{\frac{1}{2}} \tag{3-3}$$

where **U** and **d** have been defined above in (3-2).

SCHUR'S LEMMA: Any matrix which commutes with all matrices of an irreducible representation must be a constant matrix (i.e., a multiple of **E**). Thus, if a nonconstant commuting matrix exists, the representation is reducible, whereas if none exists, the representation is irreducible.

PROOF: On the basis of our first lemma, we can restrict our attention to unitary representations. Let **M** be a matrix which commutes with all matrices of the representation. Then

$$\mathbf{A}_i\mathbf{M} = \mathbf{M}\mathbf{A}_i \qquad i = 1, 2, \ldots, h$$

and taking the adjoint of both sides,

$$\mathbf{M}^{\dagger}\mathbf{A}_i{}^{\dagger} = \mathbf{A}_i{}^{\dagger}\mathbf{M}^{\dagger}$$

Pre- and postmultiplying the second of these by $\mathbf{A}_i$ leads to

$$\mathbf{A}_i\mathbf{M}^\dagger = \mathbf{M}^\dagger\mathbf{A}_i$$

Thus, if $\mathbf{M}$ commutes, $\mathbf{M}^\dagger$ also commutes. From this, it follows that the two Hermitian matrices $\mathbf{H}_1 = \mathbf{M} + \mathbf{M}^\dagger$ and $\mathbf{H}_2 = i(\mathbf{M} - \mathbf{M}^\dagger)$ also commute with all $\mathbf{A}_i$. If we can now show that a commuting Hermitian matrix is a constant, then it follows that $\mathbf{M} = \mathbf{H}_1 - i\mathbf{H}_2$ is also a constant.

Confining our attention to Hermitian commuting matrices, we can always reduce them to diagonal form by a unitary transformation: $\mathbf{d} = \mathbf{U}^{-1}\mathbf{M}\mathbf{U}$. If we define a transformed $\mathbf{A}_i' = \mathbf{U}^{-1}\mathbf{A}_i\mathbf{U}$, then

$$\mathbf{A}_i'\mathbf{d} = \mathbf{d}\mathbf{A}_i'$$

by the invariance of matrix equations under unitary transformations. We now must show that $\mathbf{d}$ is not only diagonal but also constant. To do this, consider the $\mu\nu$ element of the matrix, namely,

$$(A_i')_{\mu\nu}d_{\nu\nu} = d_{\mu\mu}(A_i')_{\mu\nu}$$

or

$$(A_i')_{\mu\nu}(d_{\nu\nu} - d_{\mu\mu}) = 0 \qquad i = 1, 2, \ldots, h$$

Now, if $d_{\nu\nu} \neq d_{\mu\mu}$, so that the matrix is not constant, then $(A_i')_{\mu\nu}$ must be zero for all A_i' and our transformation U has brought A_i to block form, showing that the representation was in fact reducible. On the other hand, if we assume the representation was irreducible, then it follows that $d_{\nu\nu} = d_{\mu\mu}$ and any commuting matrix must be a constant.

LEMMA: If we are given two irreducible representations of the same group $\mathbf{\Gamma}^{(1)}(A_i)$ and $\mathbf{\Gamma}^{(2)}(A_i)$ of dimensionality l_1 and l_2, and if a rectangular matrix $\mathbf{M}$ exists such that

$$\mathbf{M}\mathbf{\Gamma}^{(1)}(A_i) = \mathbf{\Gamma}^{(2)}(A_i)\mathbf{M} \qquad i = 1, 2, \ldots, h \tag{3-4}$$

then (1) if $l_1 \neq l_2$, $\mathbf{M} = \mathbf{0}$, or (2) if $l_1 = l_2$, $\mathbf{M} = \mathbf{0}$, or else $|\mathbf{M}| \neq 0$. In the latter case, $\mathbf{M}$ has an inverse, $\mathbf{M}\mathbf{\Gamma}^{(1)}(A_i)\mathbf{M}^{-1} = \mathbf{\Gamma}^{(2)}(A_i)$, and the two representations are equivalent.

PROOF: As shown in the first lemma, we may confine our attention to unitary representations. Also, we may assume $l_1 \leq l_2$ without loss of generality. Then, taking the adjoint of (3-4), we have

$$\mathbf{\Gamma}^{(1)}(A_i)^\dagger\mathbf{M}^\dagger = \mathbf{M}^\dagger\mathbf{\Gamma}^{(2)}(A_i)^\dagger$$

or

$$\mathbf{\Gamma}^{(1)}(A_i^{-1})\mathbf{M}^\dagger = \mathbf{M}^\dagger\mathbf{\Gamma}^{(2)}(A_i^{-1}) \tag{3-5}$$

by the unitary property which implies $\mathbf{\Gamma}^{(1)}(A_i)^\dagger = \mathbf{\Gamma}^{(1)}(A_i)^{-1} = \mathbf{\Gamma}^{(1)}(A_i^{-1})$. If we now premultiply both sides of (3-5) by $\mathbf{M}$ and use the fact that (3-4) holds for A_i^{-1} as well as A_i, since it holds for all group elements, we find

$$\mathbf{\Gamma}^{(2)}(A_i^{-1})\mathbf{M}\mathbf{M}^\dagger = \mathbf{M}\mathbf{M}^\dagger\mathbf{\Gamma}^{(2)}(A_i^{-1}) \tag{3-6}$$

Thus the matrix $\mathbf{MM}^\dagger$ commutes with all the matrices of the representation and hence must be a multiple of the unit matrix, by Schur's lemma. That is,

$$\mathbf{MM}^\dagger = c\mathbf{E} \tag{3-7}$$

Consider first the case when $l_1 = l_2$, so that $\mathbf{M}$ is a square matrix. Taking the determinant of (3-7) then yields $|\mathbf{M}|^2 = c^{l_1}$. Now, if $c \neq 0$, $|\mathbf{M}| \neq 0$, $\mathbf{M}$ has an inverse and the two representations are equivalent. On the other hand, if $c = 0$, then $\mathbf{MM}^\dagger = \mathbf{0}$. In terms of components, this means that $\sum_\lambda M_{\mu\lambda}M_{\lambda\nu}{}^\dagger = \sum_\lambda M_{\mu\lambda}M_{\nu\lambda}{}^* = 0$, for all μ and ν. Taking in particular $\mu = \nu$, we have $\sum_\lambda |\mathbf{M}_{\mu\lambda}|^2 = 0$, which is possible only if all $M_{\mu\lambda} = 0$, or in other words, if $\mathbf{M} = \mathbf{0}$.

Now consider the case when $l_1 < l_2$, so that $\mathbf{M}$ has l_1 columns and l_2 rows. We can fill $\mathbf{M}$ out to a square $l_2 \times l_2$ matrix $\mathbf{N}$ by inserting $(l_2 - l_1)$ columns of zeros. Inspection then shows that $\mathbf{NN}^\dagger = \mathbf{MM}^\dagger$. Since $\mathbf{N}$ clearly has zero determinant, so does $\mathbf{NN}^\dagger$ and hence $\mathbf{MM}^\dagger$. But by (3-7) $\mathbf{MM}^\dagger$ is a constant matrix, which we now see has $c = 0$, since the determinant vanishes. From this it follows that $\mathbf{M} = \mathbf{0}$. This completes the full proof of our lemma.

The great orthogonality theorem. If we consider all the *inequivalent, irreducible, unitary* representations of a group, then

$$\sum_R \Gamma^{(i)}(R)^*_{\mu\nu}\Gamma^{(j)}(R)_{\alpha\beta} = \frac{h}{l_i}\,\delta_{ij}\delta_{\mu\alpha}\delta_{\nu\beta} \qquad \blacktriangleright \tag{3-8}$$

where in the summation R runs over all group elements $E, A_2, \ldots, A_h$ and l_i is the dimensionality of $\Gamma^{(i)}$.

PROOF: We first consider the case of two inequivalent representations $\boldsymbol{\Gamma}^{(1)}$ and $\boldsymbol{\Gamma}^{(2)}$. Then we may construct a matrix $\mathbf{M}$ satisfying our third lemma by forming

$$\mathbf{M} = \sum_R \boldsymbol{\Gamma}^{(2)}(R)\mathbf{X}\boldsymbol{\Gamma}^{(1)}(R^{-1})$$

where $\mathbf{X}$ is a completely arbitrary matrix having l_1 columns and l_2 rows. To show that this $\mathbf{M}$ satisfies (3-4), take

$$\begin{aligned}
\boldsymbol{\Gamma}^{(2)}(S)\mathbf{M} &= \sum_R \boldsymbol{\Gamma}^{(2)}(S)\boldsymbol{\Gamma}^{(2)}(R)\mathbf{X}\boldsymbol{\Gamma}^{(1)}(R^{-1}) \\
&= \sum_R \boldsymbol{\Gamma}^{(2)}(S)\boldsymbol{\Gamma}^{(2)}(R)\mathbf{X}\boldsymbol{\Gamma}^{(1)}(R^{-1})\boldsymbol{\Gamma}^{(1)}(S^{-1})\boldsymbol{\Gamma}^{(1)}(S) \\
&= \sum_R \boldsymbol{\Gamma}^{(2)}(SR)\mathbf{X}\boldsymbol{\Gamma}^{(1)}(R^{-1}S^{-1})\boldsymbol{\Gamma}^{(1)}(S) \\
&= [\sum_R \boldsymbol{\Gamma}^{(2)}(SR)\mathbf{X}\boldsymbol{\Gamma}^{(1)}(SR)^{-1}]\boldsymbol{\Gamma}^{(1)}(S) \\
&= [\sum_R \boldsymbol{\Gamma}^{(2)}(R)\mathbf{X}\boldsymbol{\Gamma}^{(1)}(R^{-1})]\boldsymbol{\Gamma}^{(1)}(S)
\end{aligned}$$

by the rearrangement theorem; so finally

$$\mathbf{\Gamma}^{(2)}(S)\mathbf{M} = \mathbf{M}\mathbf{\Gamma}^{(1)}(S)$$

Therefore, our lemma shows that $\mathbf{M} = \mathbf{0}$. But then

$$M_{\alpha\mu} = 0 = \sum_R \sum_{\kappa\lambda} \Gamma^{(2)}(R)_{\alpha\kappa} X_{\kappa\lambda} \Gamma^{(1)}(R^{-1})_{\lambda\mu}$$

Since $\mathbf{X}$ is arbitrary, we may set all $X_{\kappa\lambda} = 0$ except $X_{\beta\nu} = 1$. Then

$$\sum_R \Gamma^{(2)}(R)_{\alpha\beta} \Gamma^{(1)}(R^{-1})_{\nu\mu} = 0 \tag{3-9}$$

Using the unitary property of $\mathbf{\Gamma}^{(1)}$, we have the equivalent form

$$\sum_R \Gamma^{(1)}(R)^*_{\mu\nu} \Gamma^{(2)}(R)_{\alpha\beta} = 0 \tag{3-9a}$$

which completes the proof of the δ_{ij} factor in (3-8).

Next we consider the case when $i = j = 1$, say. In analogy with the previous paragraph, we may construct a matrix $\mathbf{M}$ which commutes with all matrices of the representation by forming

$$\mathbf{M} = \sum_R \mathbf{\Gamma}^{(1)}(R)\mathbf{X}\mathbf{\Gamma}^{(1)}(R^{-1})$$

Then by Schur's lemma $\mathbf{M} = c\mathbf{E}$. Thus, taking the $\mu\mu'$ element,

$$\sum_{\kappa,\lambda} \sum_R \Gamma^{(1)}(R)_{\mu\kappa} X_{\kappa\lambda} \Gamma^{(1)}(R^{-1})_{\lambda\mu'} = c\delta_{\mu\mu'}$$

Choosing $X_{\kappa\lambda} = 0$ except $X_{\nu\nu'} = 1$ reduces this to

$$\sum_R \Gamma^{(1)}(R)_{\mu\nu} \Gamma^{(1)}(R^{-1})_{\nu'\mu'} = c_{\nu\nu'} \delta_{\mu\mu'} \tag{3-10}$$

We have put subscripts on the constant c to indicate the particular choice of $\mathbf{X}$. Now, choose $\mu' = \mu$, and sum on μ. This yields, on interchanging the order of the factors,

$$\sum_R \sum_\mu \Gamma^{(1)}(R^{-1})_{\nu'\mu} \Gamma^{(1)}(R)_{\mu\nu} = c_{\nu\nu'} \sum_\mu \delta_{\mu\mu}$$

or

$$\sum_R \Gamma^{(1)}(R^{-1}R)_{\nu'\nu} = l_1 c_{\nu\nu'}$$

since μ runs over the l_1 rows of the $\Gamma^{(1)}$ representation. We may reduce the left member further by noting that

$$\sum_R \Gamma^{(1)}(R^{-1}R)_{\nu'\nu} = \sum_R \Gamma^{(1)}(E)_{\nu'\nu} = h\Gamma^{(1)}(E)_{\nu'\nu} = h\delta_{\nu'\nu}$$

Therefore $c_{\nu\nu'} = h\delta_{\nu'\nu}/l_1$. Substituting back into (3-10), we have

$$\sum_R \Gamma^{(1)}(R)_{\mu\nu} \Gamma^{(1)}(R^{-1})_{\nu'\mu'} = \frac{h}{l_1} \delta_{\mu'\mu} \delta_{\nu'\nu} \tag{3-11}$$

By using the unitary property of $\mathbf{\Gamma}^{(1)}$, this becomes

$$\sum_R \Gamma^{(1)}(R)^*_{\mu'\nu'}\Gamma^{(1)}(R)_{\mu\nu} = \frac{h}{l_1}\,\delta_{\mu'\mu}\delta_{\nu'\nu} \tag{3-11a}$$

Combining (3-9*a*) and (3-11*a*), we have proved the general theorem (3-8). Moreover, (3-9) and (3-11) provide a generalization of (3-8) for nonunitary representations.

Geometric interpretation. To appreciate the significance of this result, it is helpful to interpret it as stating the orthogonality of a set of vectors in "group-element space." This is an h-dimensional vector space in which the axes or components are labeled by the various group elements $R = E, A_2, \ldots, A_h$. The vectors themselves are labeled by three indices—the representation index i and the subscripts $\mu\nu$, indicating row and column within the representation matrix. The theorem then states that all these vectors are mutually orthogonal in this h-dimensional space.

From this result we may readily draw an extremely important conclusion. If we count up the number of these orthogonal vectors, we find $\sum_i l_i^2$, where i runs over all the distinct irreducible representations, since there are l_i^2 entries in a matrix of dimensionality l_i. But clearly the maximum number of orthogonal vectors in an h-dimensional vector space is just h. Thus it follows that $\sum_i l_i^2 \leq h$. In fact we shall soon prove that the equality always holds. This gives us the dimensionality theorem

$$\sum_i l_i^2 = h \qquad \blacktriangleright \tag{3-12}$$

which is essential for working out the irreducible representations of any group. For example, in our example group of order 6, we have $h = 6$, and we have already found three irreducible representations—one of dimensionality 2 and two of dimensionality 1. Since $2^2 + 1^2 + 1^2 = 6$, this simple theorem tells us that it is impossible for any other distinct irreducible representations to exist.

3-3 The Character of a Representation

Because all matrix representations related to each other through unitary transformations are equivalent, it is clear that there is a large degree of arbitrariness in the actual forms of the matrices. This makes it worthwhile to seek a way of characterizing any given representation which is invariant under such transformations. This immediately suggests using the traces of the matrices, since these are invariant. Accordingly, we define the *character* of the jth representation as being the set of h numbers $\chi^{(j)}(E)$, $\chi^{(j)}(A_2), \ldots, \chi^{(j)}(A_h)$, where

$$\chi^{(j)}(R) = \text{Tr}\,\mathbf{\Gamma}^{(j)}(R) = \sum_{\mu=1}^{l_j} \Gamma^{(j)}(R)_{\mu\mu} \tag{3-13}$$

Since the matrix representations of all elements in the same class are related by similarity transformations (by definition of conjugate group elements), the invariance of traces shows that all elements in the same class have the same character. This enables us to specify the character of any given representation by simply giving the trace of one matrix from each class of group elements. We denote this by $\chi^{(j)}(\mathscr{C}_k)$ for the kth class.

We can profitably apply the orthogonality theorem to the character in the following way. If we set $\nu = \mu$ and $\beta = \alpha$ in Eq. (3-8), we have

$$\sum_R \Gamma^{(i)}(R)^*_{\mu\mu}\Gamma^{(j)}(R)_{\alpha\alpha} = \frac{h}{l_i}\delta_{ij}\delta_{\mu\alpha}$$

Now summing over μ and α and use of (3-13) yields

$$\sum_R \chi^{(i)}(R)^*\chi^{(j)}(R) = \frac{h}{l_i}\delta_{ij}\sum_{\mu\alpha}\delta_{\mu\alpha}$$

$$= h\delta_{ij} \qquad (3\text{-}14)$$

Thus, the characters form a set of orthogonal vectors in group-element space. Collecting the group elements according to classes, within which the $\chi^{(j)}(R)$ are the same, we can rewrite (3-14) as

$$\sum_k \chi^{(i)}(\mathscr{C}_k)^*\chi^{(j)}(\mathscr{C}_k)N_k = h\delta_{ij} \qquad ▶ \ (3\text{-}15)$$

where N_k is the number of elements in the class $\mathscr{C}_k$ and the sum now runs over *classes*.

Written in the form (3-15), our result shows that the characters of the various irreducible representations also form an orthogonal vector system in the vector space where axes are labeled by classes $\mathscr{C}_k$ rather than group elements R. Since the number of mutually orthogonal vectors in a space cannot exceed its dimensionality, it follows that the number of irreducible representations cannot exceed the number of classes. In fact it can be shown that they are always equal. Thus,

Number of irreducible representations = number of classes ▶ (3-16)

This rule, together with (3-12), enables us to work out the number and dimensionality of the irreducible representations from the numbers of group elements and classes. Thus these numerological results are of great importance in applications. Applying them to our example group of order 6, we recall that there are three classes: $\mathscr{C}_1 = E$; $\mathscr{C}_2 = A, B, C$; and $\mathscr{C}_3 = D, F$. By (3-16), this implies that there are just three irreducible representations. Then, since $2^2 + 1^2 + 1^2 = 6$ is the only solution of (3-12) for the case in which the sum of three squares must equal 6, we conclude that there must be one two-dimensional and two one-dimensional irreducible representations. Of course we already had noted these results for this case, but the method is very effective in more difficult examples where the representations are by no means obvious.

Character tables. It is convenient to display the characters of the various representations in a *character table* for any given group. The columns are labeled by the various classes, preceded by the number N_k of elements in the class. The rows are labeled by the irreducible representations, and the entries in the table are the $\chi^{(j)}(\mathscr{C}_k)$. Thus in our example group we have the table

	$\mathscr{C}_1$	$3\mathscr{C}_2$	$2\mathscr{C}_3$
$\Gamma^{(1)}$	1	1	1
$\Gamma^{(2)}$	1	-1	1
$\Gamma^{(3)}$	2	0	-1

as may be verified by using the explicit representations noted in Sec. 3-1. Note that the rows of the table are orthogonal if we use the N_k weighting factors as prescribed by (3-15). We also note that the columns form orthogonal vectors. This is not an accident, and we now proceed to prove it to be true in general.

Second orthogonality relation for characters. Since the number of classes equals the number of irreducible representations, we may form a square matrix $\mathbf{Q}$ which has the same form as the character table, namely,

$$\mathbf{Q} = \begin{pmatrix} \chi^{(1)}(\mathscr{C}_1) & \chi^{(1)}(\mathscr{C}_2) & \cdots \\ \chi^{(2)}(\mathscr{C}_1) & \chi^{(2)}(\mathscr{C}_2) & \cdots \\ \cdots\cdots & \cdots\cdots & \cdots \end{pmatrix}$$

Now consider the related matrix $\mathbf{Q}'$ defined by

$$\mathbf{Q}' = \begin{pmatrix} \dfrac{\chi^{(1)}(\mathscr{C}_1)^* N_1}{h} & \dfrac{\chi^{(2)}(\mathscr{C}_1)^* N_1}{h} & \cdots \\ \dfrac{\chi^{(1)}(\mathscr{C}_2)^* N_2}{h} & \dfrac{\chi^{(2)}(\mathscr{C}_2)^* N_2}{h} & \cdots \\ \cdots\cdots & \cdots\cdots & \cdots \end{pmatrix}$$

Then a typical element of the product is

$$(\mathbf{Q}\mathbf{Q}')_{ij} = \sum_k \frac{\chi^{(i)}(\mathscr{C}_k)\chi^{(j)}(\mathscr{C}_k)^* N_k}{h} = \delta_{ij}$$

by the first orthogonality relation for characters, (3-15). Thus $\mathbf{Q}' = \mathbf{Q}^{-1}$. But any matrix commutes with its inverse. Therefore, we also must have

$(\mathbf{Q}'\mathbf{Q})_{ij} = \delta_{ij}$. Carrying out the multiplication in the reverse order leads directly to our result,

$$\sum_i \chi^{(i)}(\mathscr{C}_k)^*\chi^{(i)}(\mathscr{C}_l) = \frac{h}{N_k}\delta_{kl} \qquad ▶ (3\text{-}17)$$

Since (3-17) is actually a direct consequence of (3-15), it contains no fundamentally new information. However, as we shall see directly, it is often a convenient aid in setting up character tables by inspection.

3-4 Construction of Character Tables

Although the character table gives much less information about a group than would a complete set of matrices for the irreducible representations, it does give enough information for many purposes. Thus it is highly desirable to be able to obtain the character table of a group directly, without first working out explicit representation matrices. In fact, in the simple cases of most interest it is possible to work out the table by inspection with the aid of a few simple rules based on the results of the previous sections. These rules are collected here for convenience.

1. The *number* of irreducible representations equals the number of classes of group elements. The latter is easily found by considering the nature of the operations or, more mechanically, by computing conjugate elements with the aid of the group-multiplication table.

2. The *dimensionalities* l_i of the irreducible representations are then determined by the fact that $\sum_i l_i^2 = h$. In most cases this has a unique solution. Since the identity element must be represented by a unit matrix, the trace of a matrix of the identity class is simply l_i. This determines the first column of the table, $\chi^{(i)}(E) = l_i$. Also, since we always have the one-dimensional representation (referred to as *totally symmetric*, *identical*, or *invariant*) in which each group element is represented by unity, we can always fill in the first row by $\chi^{(1)}(\mathscr{C}_k) = 1$.

3. The rows of the table must be orthogonal and normalized to h, with weighting factor N_k, the number of elements in $\mathscr{C}_k$. That is,

$$\sum_k \chi^{(i)}(\mathscr{C}_k)^*\chi^{(j)}(\mathscr{C}_k)N_k = h\delta_{ij} \qquad (3\text{-}15)$$

4. The columns of the table must be orthogonal vectors normalized to h/N_k. That is,

$$\sum_i \chi^{(i)}(C_k)^*\chi^{(i)}(\mathscr{C}_l) = \frac{h}{N_k}\delta_{kl} \qquad (3\text{-}17)$$

5. Elements within the ith row are related by

$$N_j\chi^{(i)}(\mathscr{C}_j)N_k\chi^{(i)}(\mathscr{C}_k) = l_i\sum_l c_{jkl}N_l\chi^{(i)}(\mathscr{C}_l) \qquad (3\text{-}18)$$

where the c_{jkl} are the constants defined by the expression governing class multiplication $\mathscr{C}_j\mathscr{C}_k = \sum_l c_{jkl}\mathscr{C}_l$. These constants may be determined given the group-multiplication table, as explained in Sec. 2-9.

PROOF: Recall that any class satisfies $X^{-1}\mathscr{C}_k X = \mathscr{C}_k$ or, equivalently, $\mathscr{C}_k X = X\mathscr{C}_k$, for all X. Now consider this equation in terms of a matrix representation. If we introduce the matrix $\mathscr{C}_k$, which is the sum of the matrices of all the elements in the class $\mathscr{C}_k$, then it follows that $\mathscr{C}_k\mathbf{X} = \mathbf{X}\mathscr{C}_k$, because matrix multiplication by $\mathbf{X}$ is linear and matrix addition is commutative. But if this is so, Schur's lemma states that $\mathscr{C}_k$ must be a constant matrix, say, $\eta_k\mathbf{E}$. In this case, one readily sees that the matrix form of the equation defining the c_{jkl} reduces to $\eta_j\eta_k = \sum_l c_{jkl}\eta_l$. We now evaluate η_k by taking the trace of $\mathscr{C}_k$ in two ways and comparing, namely,

$$\operatorname{Tr} \mathscr{C}_k = \operatorname{Tr} \eta_k\mathbf{E} = \eta_k l_i$$

and

$$\operatorname{Tr} \mathscr{C}_k = \operatorname{Tr} \sum_{\mu=1}^{N_k} \mathbf{A}_\mu = N_k\chi^{(i)}(\mathscr{C}_k)$$

Thus

$$\eta_k = \frac{N_k\chi^{(i)}(\mathscr{C}_k)}{l_i}$$

and rule 5 follows directly.

The first three rules usually suffice to work out a character table, but the last two often facilitate the process of inspection. For example, by use of these rules the complete character table for the group of the equilateral triangle, as given above, could be quickly found without any knowledge of the explicit matrices at all. The first row and column are fixed by rule 2, and the four integers to complete the table so as to satisfy rules 3 and 4 are readily picked out. In case the characters should be nonintegral, as may occur in various instances, the procedure is less simple. However, if a set of integers satisfying the rules can be found, one may normally take it to be the proper character table.

3-5 Decomposition of Reducible Representations

Clearly the character of a reducible representation Γ is the sum of the characters of the component irreducible representations $\Gamma^{(j)}$. This can be seen by supposing that the representation has been brought into block form by a suitable similarity transformation. In that case, the trace of the large matrix is simply the sum of the traces of the submatrices in the blocks along the diagonal. Thus we can write

$$\chi(R) = \sum_j a_j\chi^{(j)}(R) \tag{3-19}$$

where χ is the character of Γ and a_j is the number of times $\Gamma^{(j)}$ appears in Γ. Since the $\chi^{(j)}(R)$ form an orthogonal vector system, the expansion coefficients a_i can be determined as usual by taking the scalar product with $\chi^{(i)}(R)$. Thus, using (3-14),

$$\sum_R \chi(R)\chi^{(i)}(R)^* = \sum_R \sum_j a_j \chi^{(j)}(R)\chi^{(i)}(R)^* = ha_i$$

and therefore

$$a_j = h^{-1}\sum_R \chi^{(j)}(R)^*\chi(R) = h^{-1}\sum_k N_k \chi^{(j)}(\mathscr{C}_k)^*\chi(\mathscr{C}_k) \qquad \blacktriangleright \; (3\text{-}20)$$

We conclude that the number of times the various irreducible representations appear in a given reducible representation is uniquely determined by the character of the reducible representation, assuming that the character table of the group is known. We shall find this result central to the enumeration of residual degeneracies when a representation is rendered reducible by decreasing the size of the symmetry group.

The regular representation. Given the multiplication table of a group, we can always form a reducible representation called the *regular representation* as follows: Write down the multiplication table, rearranging rows so that they correspond to the *inverses* of the elements labeling the columns. In this way one naturally obtains only the identity element E along the principal diagonal. The matrix of the regular representation for the group element R is then obtained by replacing R by unity and all other elements by zero in the resulting table. For our example group, the rearranged multiplication table and a typical matrix of $\Gamma^{(\text{reg})}$ are shown below:

	E	A	B	C	D	F
E^{-1}	E	A	B	C	D	F
A^{-1}	A	E	D	F	B	C
B^{-1}	B	F	E	D	C	A
C^{-1}	C	D	F	E	A	B
D^{-1}	F	B	C	A	E	D
F^{-1}	D	C	A	B	F	E

$$\Gamma^{(\text{reg})}(A) = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix}$$

Evidently, in general $\chi^{(\text{reg})}(E) = h$, and $\chi^{(\text{reg})}(R) = 0$ for $R \neq E$, since by construction only $\Gamma^{(\text{reg})}(E)$ has nonzero elements on the diagonal, and it has unity h times.

Before proceeding, we should confirm that the matrices defined above do in fact form a representation. That is, we must show that

$$\Gamma^{(\text{reg})}(BC) = \Gamma^{(\text{reg})}(B)\Gamma^{(\text{reg})}(C)$$

or in component form

$$\Gamma^{(\text{reg})}(BC)_{A_k^{-1}A_i} = \sum_{A_j} \Gamma^{(\text{reg})}(B)_{A_k^{-1}A_j}\Gamma^{(\text{reg})}(C)_{A_j^{-1}A_i}$$

where the subscripts label the rows and columns in the rearranged multiplication table. By construction, we know that

$$\Gamma^{(\mathrm{reg})}(B)_{A_k^{-1}A_j} = \begin{cases} 1 & \text{if } A_k^{-1}A_j = B \\ 0 & \text{otherwise} \end{cases}$$

and a similar relation holds for $\Gamma^{(\mathrm{reg})}(C)$. Thus the indicated sum over A_j will vanish unless for some A_j both $\Gamma^{(\mathrm{reg})}(B)_{A_k^{-1}A_j}$ and $\Gamma^{(\mathrm{reg})}(C)_{A_j^{-1}A_i}$ are simultaneously nonzero. This will occur if, and only if,

$$BC = (A_k^{-1}A_j)(A_j^{-1}A_i) = A_k^{-1}A_i,$$

in which case the sum equals unity. But this coincides with the definition of the left member $\Gamma^{(\mathrm{reg})}(BC)_{A_k^{-1}A_i}$. Hence the matrices defined above do form a representation.

CELEBRATED THEOREM: This theorem states that the regular representation contains each irreducible representation a number of times equal to the dimensionality of the irreducible representation.

PROOF: We apply our formula (3-20) for the decomposition of representations. Thus a_j, the number of times $\Gamma^{(j)}$ appears in $\Gamma^{(\mathrm{reg})}$, is given by

$$\begin{aligned} a_j &= h^{-1} \sum_R \chi^{(j)}(R)^* \chi^{(\mathrm{reg})}(R) \\ &= h^{-1}\chi^{(j)}(E)h \\ &= l_j \end{aligned}$$

We now use this theorem to prove that the equality sign in (3-12) must in fact hold. By construction, the dimensionality of the regular representation is equal to h, the order of the group. But it also must equal the sum of the dimensionalities of all the irreducible representations of which it is composed. By the celebrated theorem, the latter is $\sum_j l_j \times l_j = \sum_j l_j^2$. Therefore,

$$\sum_j l_j^2 = h$$

This result removes the possible inequality sign left in our earlier argument based simply on the number of possible orthogonal vectors in a space of given dimension.

3-6 Application of Representation Theory in Quantum Mechanics

Transformation operators. Let us now depart from our formal development of the theory of group representations to examine the relation of this theory to quantum mechanics, which provides our reason for presenting the theory in the first place. In the applications which we shall consider, the group of interest is the group of symmetry operators which leave the

Hamiltonian of the problem invariant. Each such operator can be specified by giving a real orthogonal transformation of coordinates **R** such that the new coordinates **x**′ are related to the original ones **x** by

$$\mathbf{x}' = \mathbf{R}\mathbf{x} \tag{3-21}$$

or in terms of components

$$x_i' = \sum_j R_{ij} x_j$$

Depending on the particular form of **R**, it may represent a rotation of coordinates, a reflection, an inversion, or any combination of these. In all these cases, **R** is a real orthogonal matrix, and hence $\mathbf{R}^{-1} = \mathbf{R}^{\dagger} = \tilde{\mathbf{R}}$, where $\tilde{\mathbf{R}}$ is the transpose of **R**. Thus we can write the inverse transformation as

$$x_i = \sum_j R^{-1}{}_{ij} x_j' = \sum_j R_{ji} x_j'$$

As discussed earlier, such a set of matrices **R** form a group under matrix multiplication. Although the present discussion will be given in the language of such orthogonal transformations, the results are readily carried over when the symmetry operations include, e.g., permutation of the coordinates of identical particles and translation of coordinates.

For our purposes, we now introduce a new group isomorphic to this group of coordinate transformations, in which the group elements are transformation operators which operate on *functions* rather than *coordinates*. We denote the operator which corresponds to **R** by P_R and follow Wigner's convention in defining P_R by requiring that the following be satisfied identically in **x**:

$$P_R f(\mathbf{R}\mathbf{x}) = f(\mathbf{x})$$

Equivalently,

$$P_R f(\mathbf{x}) = f(\mathbf{R}^{-1}\mathbf{x}) \tag{3-22}$$

That is, P_R changes the functional form of $f(\mathbf{x})$ in such a way as to compensate for the change of variable **R**.

As an example, let **R** be the transformation to X', Y', Z' axes rotated by 90° about the X axis. Then $x' = x$, $y' = z$, $z' = -y$, and the matrices concerned are

$$\mathbf{R} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \qquad \mathbf{R}^{-1} = \tilde{\mathbf{R}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}$$

Thus

$$\mathbf{R}^{-1}\mathbf{x} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ -z \\ y \end{pmatrix}$$

and from our definition above

$$P_R f(x, y, z) = P_R f(\mathbf{x}) = f(\mathbf{R}^{-1}\mathbf{x}) = f(x, -z, y)$$

For example, if we let this P_R operate on the three orthogonal p-like functions for an atom with nucleus at the origin, we obtain

$$P_R\{x\varphi(r)\} = x\varphi(r)$$
$$P_R\{y\varphi(r)\} = -z\varphi(r)$$
$$P_R\{z\varphi(r)\} = y\varphi(r)$$

since $r = (x^2 + y^2 + z^2)^{\frac{1}{2}}$ is invariant under such a rotation. We note that the contours of these functions are rotated clockwise with respect to the axes, whereas the axes are rotated counterclockwise. These two rotations compensate, as required by the definition of P_R, and one can consider the operation from either point of view. However, we shall emphasize the viewpoint in which the transformation operator P_R rotates the contours of the function, so that we minimize the chance of confusion with several sets of coordinate axes.

Before proceeding, let us verify that the group of operators P_R is in fact isomorphic to the group of coordinate transformations **R**. To see this, we need to show that

$$P_S P_R = P_{SR}$$

where S and R are two transformations. We consider the successive operations in detail. First,

$$P_R f(\mathbf{x}) = f(\mathbf{R}^{-1}\mathbf{x}) = g(\mathbf{x})$$

where $g(\mathbf{x})$ is the new function which incorporates the effect of $\mathbf{R}^{-1}$ into the functional form. [In our example above, if $f(\mathbf{x}) = y\varphi(r)$, then $g(\mathbf{x}) = -z\varphi(r)$.] Now we apply the second operator P_S, obtaining

$$P_S[P_R f(\mathbf{x})] = P_S g(\mathbf{x}) = g(\mathbf{S}^{-1}\mathbf{x}) = f[\mathbf{R}^{-1}(\mathbf{S}^{-1}\mathbf{x})]$$
$$= f[(\mathbf{SR})^{-1}\mathbf{x}] = P_{SR} f(\mathbf{x})$$

Thus the transformation P_{SR} arising from the product SR is the product of the transformation P_S and P_R applied in the proper order.

The group of the Schrodinger equation. Now let us consider that special group of operators P_R which commute with the Hamiltonian operator H for any given problem. These will be the operators arising from transformations which leave the Hamiltonian invariant. For example, if the potential energy in an atom depends only on the distance from the nucleus and is independent of the angular coordinates, then any rotation or reflection leaves the potential unchanged. To illustrate precisely what we mean by this, consider a simple Coulomb potential $V = -e^2/r = -e^2/(x^2 + y^2 + z^2)^{\frac{1}{2}}$. Now, under the example transformation treated above, this becomes $V = -e^2/[x^2 + (-z)^2 + y^2]^{\frac{1}{2}}$, which is in fact the same as the expression with which we began. A similar argument could be applied to the kinetic energy operator $-(\hbar^2/2m)(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2)$. Clearly, if an operator leaves H invariant, it is immaterial whether it appears to the left or right of it, that is, $P_R H\psi = HP_R\psi$, and the two operators commute. The set of all such operators which commute with H are said to form *the group of the Schrödinger equation.* They certainly do form a group because inverse coordinate transformations exist and because the product of two operators which leave H invariant will also leave it invariant since the product simply indicates that the two operate in succession. In the alternate language, the product of two operators which commute with H will also commute with H.

If we apply one of these commuting transformation operators to the Schrodinger equation, we have

$$P_R H\psi_n = P_R E_n \psi_n$$

or

$$HP_R\psi_n = E_n P_R \psi_n$$

since P_R commutes with H and of course with the eigenvalue E_n. From this result we conclude that any function $P_R\psi_n$ obtained by operating on an eigenfunction ψ_n by a symmetry operator from the group of the Schrodinger equation will also be an eigenfunction having the same energy as the original one. Thus, given any eigenfunction, we can generate other eigenfunctions degenerate with it by application of all the symmetry operators which commute with H. If this procedure yields *all* the degenerate functions, the degeneracy is said to be *normal.* For example, given one atomic p function, we can generate the other two degenerate with it by making rotations of coordinates, which commute with the atomic Hamiltonian because of its spherical symmetry. (Depending on the particular choice of p functions, it may be necessary to use linear combinations of rotated functions, but this is a trivial extension.) Any degenerate functions which cannot be obtained in this way are said to comprise an *accidental degeneracy*, meaning one with no obvious origin in symmetry. A classical example is the degeneracy in the hydrogen atom of states of different angular momentum l but the same principal quantum number n, for example, of $2s$ and $2p$ functions. Deeper study usually shows either that the degeneracy is not exact or else that a hidden symmetry in the Hamiltonian can be found which "explains" the degeneracy. In the example of hydrogen, Fock[1] has shown that the degeneracy can be considered to arise from a four-dimensional rotational symmetry of the Hamiltonian in momentum space.

Representations. Let us assume that the eigenvalue E_n is l_n-fold degenerate (excluding any accidental degeneracies). Then we may choose a set of l_n orthonormal eigenfunctions belonging to E_n. By our result above, operation with any commuting P_R on any one of the l_n functions produces another function having the same energy, which accordingly must be expressible as a linear combination of this complete set of degenerate functions. In the language of algebra, the l_n degenerate functions form basis vectors in an l_n-dimensional vector space. This space is a subspace of the entire Hilbert space of eigenfunctions of H, a subspace invariant under all the operations of the group of the Schrodinger equation. Thus, the effect of each of these transformation operators on any function in this subspace can be represented by a matrix which can be worked out by considering the effect of the operator on each of the basis functions in turn. These matrices $\mathbf{\Gamma}$ are defined formally by

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[1] V. Fock, *Z. Physik*, **98**, 145 (1935).

$$P_R\psi_\nu^{(n)} = \sum_{\kappa=1}^{l_n} \psi_\kappa^{(n)}\Gamma^{(n)}(R)_{\kappa\nu} \tag{3-23}$$

where the sum runs over the l_n degenerate eigenfunctions $\psi_\kappa^{(n)}$ having the same energy E_n as $\psi_\nu^{(n)}$. These l_n-dimensional matrices then form an l_n-dimensional representation of the group of the Schrodinger equation. Such a representation can be based on each set of degenerate eigenfunctions. These representations are irreducible since (excluding accidental degeneracies) there is always an operator in the group which transforms each function into any other degenerate with it. Thus no smaller matrices could express the most general transformation. To prove that the matrices defined in (3-23) actually form a representation of the group, we consider two successive operations. For simplicity we suppress the index n, which denotes the particular representation.

$$\begin{aligned} P_{SR}\psi_\nu &= P_S P_R \psi_\nu = P_S \sum_\kappa \psi_\kappa \Gamma(R)_{\kappa\nu} \\ &= \sum_\kappa (P_S\psi_\kappa)\Gamma(R)_{\kappa\nu} = \sum_{\kappa,\lambda} \psi_\lambda \Gamma(S)_{\lambda\kappa}\Gamma(R)_{\kappa\nu} \\ &= \sum_\lambda \psi_\lambda [\mathbf{\Gamma}(S)\mathbf{\Gamma}(R)]_{\lambda\nu} \end{aligned}$$

But by definition of $\mathbf{\Gamma}(SR)$,

$$P_{SR}\psi_\nu = \sum_\lambda \psi_\lambda \Gamma(SR)_{\lambda\nu}$$

Therefore $$\mathbf{\Gamma}(SR) = \mathbf{\Gamma}(S)\mathbf{\Gamma}(R)$$

and the matrices do in fact form a representation of the group. Thus we conclude that *the set of l_n degenerate eigenfunctions $\psi_\nu^{(n)}$ of energy E_n form basis functions for an l_n-dimensional irreducible representation* $\Gamma^{(n)}$ *of the group of the Schrodinger equation.* One can readily show that the representation is *unitary* if one chooses an orthonormal set of basis functions.

PROOF: If we denote the Hermitian scalar product of ψ and φ by $(\psi, \varphi) = \int \psi^*\varphi \, d\tau$, and if we assume the basis functions ψ_κ to be orthonormal, then

$$\delta_{\kappa\nu} = (\psi_\kappa, \psi_\nu) = (P_R\psi_\kappa, P_R\psi_\nu)$$

since in the second form the integral may be considered simply to be carried out in a rotated coordinate system. Using the definition of the representation matrices, we find

$$\begin{aligned}\delta_{\kappa\nu} &= \Big(\sum_{\lambda} \psi_\lambda \Gamma(R)_{\lambda\kappa}, \sum_{\mu} \psi_\mu \Gamma(R)_{\mu\nu}\Big) \\ &= \sum_{\lambda,\mu} (\psi_\lambda, \psi_\mu) \Gamma(R)^*_{\lambda\kappa} \Gamma(R)_{\mu\nu} \\ &= \sum_{\lambda} \Gamma(R)^*_{\lambda\kappa} \Gamma(R)_{\lambda\nu} = \sum_{\lambda} \Gamma(R)^\dagger_{\kappa\lambda} \Gamma(R)_{\lambda\nu} \\ &= [\mathbf{\Gamma}(R)^\dagger \mathbf{\Gamma}(R)]_{\kappa\nu}\end{aligned}$$

Thus $\mathbf{\Gamma}(R)^\dagger \mathbf{\Gamma}(R) = \mathbf{E}$, and the matrix representation is unitary.

Group theory and quantum numbers. Finally, let us consider the effect of choosing a different set of linearly independent basis functions ψ'_ν which are linear combinations of the first set. That is,

$$\psi'_\mu = \sum_{\nu=1}^{l} \psi_\nu \alpha_{\nu\mu} \qquad \text{or} \qquad \psi_\kappa = \sum_{\lambda=1}^{l} \psi'_\lambda \alpha^{-1}{}_{\lambda\kappa}$$

Then

$$\begin{aligned}P_R \psi'_\mu &= P_R \sum_{\nu} \psi_\nu \alpha_{\nu\mu} = \sum_{\kappa,\nu} \psi_\kappa \Gamma(R)_{\kappa\nu} \alpha_{\nu\mu} \\ &= \sum_{\lambda,\kappa,\nu} \psi'_\lambda \alpha^{-1}{}_{\lambda\kappa} \Gamma(R)_{\kappa\nu} \alpha_{\nu\mu} = \sum_{\lambda} \psi'_\lambda [\boldsymbol{\alpha}^{-1} \mathbf{\Gamma}(R) \boldsymbol{\alpha}]_{\lambda\mu} \\ &= \sum_{\lambda} \psi'_\lambda \Gamma'(R)_{\lambda\mu}\end{aligned}$$

where $\mathbf{\Gamma}'$ is the new representation matrix. Thus we see that

$$\mathbf{\Gamma}'(R) = \boldsymbol{\alpha}^{-1} \mathbf{\Gamma}(R) \boldsymbol{\alpha} \tag{3-24}$$

and the different choice of basis functions merely produces a representation *equivalent* to the old one. Thus, within a similarity transformation, *there is a unique representation of the group of the Schrödinger equation corresponding to each eigenvalue of the Hamiltonian.* A set of eigenfunctions can always be classified uniquely according to the irreducible representation to which it belongs, i.e., the one for which the eigenfunctions form a set of basis vectors.

If a particular choice of matrices (within the range allowed by the similarity transformation) is made, then a function may be characterized even more precisely by giving its row index within the representation. In this way group theory provides "good quantum numbers" for any problem in the form of the labels of the representations and the rows within each one. The associated degeneracy is simply the dimensionality of the representation. Thus, by finding the dimensionalities of all the irreducible representations of the group of the Schrödinger equation (as described in Sec. 3-4), we are able to determine unequivocally the degrees of (nonaccidental) degeneracy possible in any problem. From this observation it follows that a perturbation can lift degeneracies if, and only if, its inclusion in the Hamiltonian reduces the symmetry group and hence changes the possible irreducible representations. Moreover, if representation matrices are worked out, they contain the transformation properties of all eigenfunctions under all the symmetry operators of the group.

An example. As an example using our standard group of order 6, imagine that we are interested in finding the eigenstates of an electron moving in the potential field of three protons located at the corners of an equilateral triangle. In this case the group of the Schrodinger equation contains all six rotational operations considered in this example group. (It also contains six more operations involving a reflection in the plane, but as we shall see later these extra operations do not affect the degeneracies.) This group has three irreducible representations of dimensionality 1, 1, and 2. Thus only nondegenerate and doubly degenerate states are possible. All higher degeneracy is excluded by group theory alone. Those eigenfunctions belonging to the identical representation $\Gamma^{(1)}$ are invariant under all the group operations. Similarly, basis functions of $\Gamma^{(2)}$ are invariant under E, D, and F, but they change sign under the 180° rotations A, B, and C. This can be seen from the character table, since for a one-dimensional representation $\chi(R) = \mathbf{\Gamma}(R)$. The doubly degenerate eigenfunctions of $\Gamma^{(3)}$ symmetry can be chosen so as to transform between themselves in accordance with the 2×2 matrix representation. For example, an eigenfunction ψ_1 belonging to the first row of $\Gamma^{(3)}$ will transform into $-\frac{1}{2}\psi_1 + (\sqrt{3}/2)\psi_2$ under P_B. Of course, a different choice of the degenerate eigenfunctions would transform according to a set of matrices related to those given above by a similarity transformation, which will also be unitary if the new linear combinations are chosen to preserve orthonormality.

3-7 Illustrative Representations of Abelian Groups

In an Abelian group, each element forms a class by itself. Therefore the number of classes, and hence the number of irreducible representations, equals the number of group elements h. But in this case, (3-12) requires that

$$\sum_{i=1}^{h} l_i^2 = h$$

This is possible only by choosing $l_1 = l_2 = \cdots = l_h = 1$. Thus *an Abelian group of order h has h one-dimensional representations and no others.* Each of these representations is simply a set of complex numbers, one number being associated with each group element. Note that the absence of any larger irreducible representations implies that there are no degeneracies if the symmetry group of the Hamiltonian is Abelian.

Cyclic groups. Cyclic groups are Abelian groups with elements $A_1 = A$, $A_2 = A^2, \ldots, A^h = E$. Let the number representing A itself in some representation of this group be denoted $\Gamma(A) = r$. Then $\Gamma(A_n) = \Gamma(A)^n = r^n$, and in particular $\Gamma(E) = 1$ requires that

$$\Gamma(A)^h = r^h = 1$$

or

$$r = e^{2\pi i p/h} \qquad p = 1, 2, 3, \ldots, h$$

since these h values of r form the hth roots of unity. In this way we have found all h of the irreducible representations. They can be written in the form

$$\Gamma^{(p)}(A) = e^{2\pi i p/h} \qquad p = 1, 2, 3, \ldots, h \qquad ▶ \text{(3-25)}$$

Bloch's theorem. The cyclic group of order h is the symmetry group of the Hamiltonian for a periodic potential with h periods in a ring or in a linear arrangement with periodic boundary conditions applied at walls h periods apart. In this application the group element A represents a displacement through one period. For definiteness, let A represent a displacement by a in coordinates (or by $-a$ in the contours of the function) so that $P_A\psi(x) = \psi(x + a)$. By our general theorem, all eigenfunctions of a Hamiltonian having this symmetry must transform according to some representation of the group. For example, all solutions from the pth representation must have the property

$$\psi_p(x + a) = P_A\psi_p(x) = \Gamma^{(p)}(A)\psi_p(x) = e^{2\pi i p/h}\psi_p(x)$$

Upon introducing the total length $L = ah$, this can be written as

$$\psi_p(x + a) = e^{2\pi i p a/L}\psi_p(x) = e^{ika}\psi_p(x)$$

where k is related to p by $k = 2\pi p/L$. Relabeling the function with the equivalent index k, we have

$$\psi_k(x + a) = e^{ika}\psi_k(x) \qquad \text{(3-26)}$$

This equation gives the transformation property imposed by the translational-symmetry group. As is easily seen, any function $\psi_k(x)$ satisfying (3-26) can be written in the form

$$\psi_k(x) = u_k(x)e^{ikx} \qquad \text{(3-27)}$$

where $u_k(x)$ is periodic with the period a. This result is the celebrated Bloch theorem of solid-state physics. Clearly it is based purely on symmetry through the machinery of group theory. Therefore it is a rigorous result, free of special approximations, and k defined in this way is a "good quantum number" for characterizing eigenfunctions for a periodic potential.

Two-dimensional rotation group. Any group composed of rotations about a fixed axis is clearly an Abelian group. If all angles of rotation φ are allowed, the group is of infinite order. However, it is so simple that we can handle it anyway. Being Abelian, its representations are just numbers. The group-multiplication property for successive rotations implies that the representations satisfy

$$\Gamma(\varphi_1)\Gamma(\varphi_2) = \Gamma(\varphi_1 + \varphi_2)$$

This can be satisfied only by an exponential relation of the sort

$$\Gamma^{(m)}(\pm\varphi) = e^{im\varphi} \tag{3-28}$$

the plus sign referring to a rotation of axes and the negative sign to a rotation of the contours of the function. We choose the latter convention in discussing rotations. The representation index m is restricted to the values $m = 0, \pm 1, \pm 2, \ldots$ by the requirement that $\Gamma^{(m)}(2\pi) = \Gamma^{(m)}(E) = 1$. It is readily verified that any function satisfying

$$\begin{aligned}\psi_m(r, \theta, \varphi - \varphi_0) &= P_{\varphi_0}\psi_m(r, \theta, \varphi)\\ &= \Gamma^{(m)}(\varphi_0)\psi_m(r, \theta, \varphi) = e^{-im\varphi_0}\psi_m(r, \theta, \varphi)\end{aligned}$$

depends on φ only through a factor $e^{im\varphi}$. Hence any eigenfunction for a Hamiltonian whose symmetry group is the group of all rotations about an axis must have the form

$$\psi_m(r, \theta, \varphi) = f(r, \theta)e^{im\varphi} \qquad m = 0, \pm 1, \pm 2, \ldots$$

This result is a familiar consequence of the fact that angular momentum along an axis of symmetry is conserved and hence has a good quantum number m associated with it.

3-8 Basis Functions for Irreducible Representations

The foregoing simple examples have given a small indication of the way in which irreducible-representation labels serve as good quantum numbers in physical applications. We now wish to develop methods for dealing with the representations of dimensionality greater than 1, which arise when the symmetry group contains noncommuting elements leading to the possibility of degeneracy. In this case we need *two* labels for a basis function, one for the irreducible representation and one for the row (or column) within the representation. Naturally the second label retains a definite significance only as long as we confine ourselves to a particular choice of representation matrices from among all the equivalent sets related by a similarity transformation.

Let a basis function belonging to the κth row of the jth irreducible representation be denoted $\varphi_\kappa^{(j)}$. The other functions $\varphi_\lambda^{(j)}$ required to complete the basis for the representation are called the *partners* of the given function. Then by definition the result of operating with any element of the group on $\varphi_\kappa^{(j)}$ can be expressed as a linear combination of $\varphi_\kappa^{(j)}$ and its partners as follows,

$$P_R\varphi_\kappa^{(j)} = \sum_{\lambda=1}^{l_j} \varphi_\lambda^{(j)}\Gamma^{(j)}(R)_{\lambda\kappa} \tag{3-29}$$

where l_j is the dimensionality of the representation. Now, if we multiply through by $\Gamma^{(i)}(R)^*_{\lambda'\kappa'}$, sum over R, and use the great orthogonality theorem (3-8), we obtain

$$\sum_R \Gamma^{(i)}(R)^*_{\lambda'\kappa'} P_R\varphi_\kappa^{(j)} = \frac{h}{l_j}\,\delta_{ij}\delta_{\kappa\kappa'}\varphi_{\lambda'}^{(j)} \tag{3-30}$$

From this equation we conclude that application of the operator

$$\mathscr{P}_{\lambda\kappa}^{(j)} = \frac{l_j}{h}\sum_R \Gamma^{(j)}(R)_{\lambda\kappa}{}^*P_R \tag{3-31}$$

to a basis function has the property of yielding zero unless the function being operated on belongs to the κth row of $\Gamma^{(j)}$. Moreover, we see that, if this condition *is* satisfied, then the result of the operation is $\varphi_\lambda^{(j)}$. This gives us a prescription for generating all the partners of any given basis function. Also, if we set $\lambda = \kappa$, we obtain

$$\mathscr{P}_{\kappa\kappa}^{(j)}\varphi_\kappa^{(j)} = \varphi_\kappa^{(j)} \tag{3-32}$$

In other words, $\varphi_\kappa^{(j)}$ is an eigenfunction of $\mathscr{P}_{\kappa\kappa}^{(j)}$ with eigenvalue unity. This property serves to identify uniquely the labels of any basis function. Note that, since $\mathscr{P}_{\kappa\kappa}^{(j)}$ is a linear operator, any linear combination of functions belonging to the κth row of $\Gamma^{(j)}$ (but coming from different choices of basis functions) such as $a\varphi_\kappa^{(j)} + b\psi_\kappa^{(j)}$ will also belong to that row and representation.

THEOREM: If $\Gamma^{(1)}, \Gamma^{(2)}, \ldots, \Gamma^{(c)}$ are all of the distinct irreducible representations of a group of operators P_R, then any function F in the space operated on by P_R can be decomposed into a sum of the form

$$F = \sum_{j=1}^{c}\sum_{\kappa=1}^{l_j} f_\kappa^{(j)} \tag{3-33}$$

where $f_\kappa^{(j)}$ belongs to the κth row of the jth irreducible representation.

PROOF: Consider the set of all functions $F, F'_2, \ldots, F'_h$ formed by operation with the operators $P_E, P_{A_2}, \ldots, P_{A_h}$ on F. Discard all functions which are not linearly independent of the others, and orthogonalize the remainder (e.g., by the Schmidt procedure). Denote the resulting set of n functions by $F, F_2, \ldots, F_n$. These functions form the basis for a unitary representation of the group, since the result of successive operations must always be expressible as a linear combination of the set. This follows since the equation $P_SP_RF = P_{SR}F$ is in the space spanned by the set, by construction.

Call this n-dimensional representation Γ, so that

$$P_R F_k = \sum_{i=1}^{n} F_i \Gamma(R)_{ik}$$

There are now two possibilities: either Γ is one of the irreducible representations, or it is not. If it is, then F has been shown to belong to a particular row of that representation and the theorem is proved. If it is not, then it can be brought to block form in terms of the chosen irreducible representation matrices by a similarity transformation, so that

$$\boldsymbol{\alpha}^{-1}\boldsymbol{\Gamma}(R)\boldsymbol{\alpha} = \begin{pmatrix} \boldsymbol{\Gamma}^{(i)}(R) & 0 & 0 \\ 0 & \boldsymbol{\Gamma}^{(j)}(R) & 0 \\ 0 & 0 & \cdots \end{pmatrix} \tag{3-34}$$

The matrix $\boldsymbol{\alpha}$ now defines a set of functions F_k'' which transform according to (3-34) and hence are functions of the type $f_\kappa^{(j)}$ for various values of j and κ. Using the inverse $\boldsymbol{\alpha}^{-1}$, we may express the F_k, and in particular F, as linear combinations of the F_k'' or $f_\kappa^{(j)}$. This completes the proof.

Having established the validity of (3-33), we may now use the operators $\mathscr{P}_{\kappa\kappa}^{(j)}$ defined in (3-31) to determine the individual terms in the sum in (3-33). We have noted that

$$\mathscr{P}_{\kappa\kappa}^{(j)} f_{\kappa'}^{(j')} = \delta_{\kappa\kappa'}\delta_{jj'} f_\kappa^{(j)} \tag{3-35}$$

Therefore

$$\mathscr{P}_{\kappa\kappa}^{(j)} F = f_\kappa^{(j)} \tag{3-36}$$

and $\mathscr{P}_{\kappa\kappa}^{(j)}$ is a *projection operator* which projects out the part of any function which belongs to the κth row of the jth representation. Such a projection operator is called *idempotent* because of the property that

$$\mathscr{P}_{\kappa\kappa}^{(j)}\mathscr{P}_{\kappa\kappa}^{(j)} = \mathscr{P}_{\kappa\kappa}^{(j)}$$

i.e., all powers of the operator are equal.

We now are able to form a set of basis functions for any representation at will. Starting with an arbitrary function F, we can project out one $f_\kappa^{(j)}$, which after normalization is a suitable basis function $\varphi_\kappa^{(j)}$. Then use of the transfer operators $\mathscr{P}_{\lambda\kappa}^{(j)}$ yields all its partners, since $\mathscr{P}_{\lambda\kappa}^{(j)}\varphi_\kappa^{(j)} = \varphi_\lambda^{(j)}$. Van Vleck has appropriately styled this procedure as the *basis-function generating machine.*

THEOREM: Two functions which belong to different irreducible representations or to different rows of the same unitary representation are orthogonal.

PROOF: Consider the scalar product

$$\begin{aligned}(\varphi_\kappa^{(j)}, \psi_{\kappa'}^{(j')}) &= (P_R\varphi_\kappa^{(j)}, P_R\psi_{\kappa'}^{(j')}) \\ &= \sum_{\lambda,\lambda'} \Gamma^{(j)}(R)^*_{\lambda\kappa}\Gamma^{(j')}(R)_{\lambda'\kappa'}(\varphi_\lambda^{(j)}, \psi_{\lambda'}^{(j')})\end{aligned}$$

We may sum the right member over all R and divide by h, since it must be independent of R. Applying the great orthogonality theorem, we obtain

$$(\varphi_\kappa^{(j)}, \psi_{\kappa'}^{(j')}) = \delta_{jj'}\delta_{\kappa\kappa'} \sum_{\lambda=1}^{l_j} (\varphi_\lambda^{(j)}, \psi_\lambda^{(j)}) l_j^{-1}$$

Thus, not only have we proved the theorem, but we have also shown that the scalar product $(\varphi_\kappa^{(j)}, \psi_\kappa^{(j)})$ is independent of κ.

The results derived above have required knowledge of the complete representation matrices $\mathbf{\Gamma}^{(j)}(R)$ or at least all the diagonal values $\Gamma^{(j)}(R)_{\kappa\kappa}$. We can get similar but less detailed results with knowledge of only the characters of the representations. To do this, we set $\lambda = \kappa$ in (3-31) and sum over κ. This defines a new projection operator

$$\mathscr{P}^{(j)} = \sum_\kappa \mathscr{P}_{\kappa\kappa}^{(j)} = \frac{l}{h} \sum_R \chi^{(j)}(R)^* P_R \tag{3-37}$$

Following arguments similar to those above, we see that any function $f^{(j)}$ expressible as a sum of functions belonging only to rows within the jth representation will satisfy $\mathscr{P}^{(j)}f^{(j)} = f^{(j)}$ and that

$$\mathscr{P}^{(j)}F = f^{(j)} \tag{3-38}$$

That is, from an arbitrary function $\mathscr{P}^{(j)}$ projects out the part belonging to the jth representation. These results are of course unaffected by similarity transformations which scramble the basis functions, and hence the rows, in any given representation.

As a rather trivial example of these results, consider the group consisting of the identity and the reflection operator σ which takes x into $-x$. This group has two classes, hence two one-dimensional irreducible representations. The character table is

	E	σ
$\Gamma^{(1)}$	1	1
$\Gamma^{(2)}$	1	-1

Hence, the projection operator for $\Gamma^{(1)}$ is $\mathscr{P}^{(1)} = (\frac{1}{2})(P_E + P_\sigma)$, and that for $\Gamma^{(2)}$ is $\mathscr{P}^{(2)} = (\frac{1}{2})(P_E - P_\sigma)$. Operating on an arbitrary function $F(x)$, these yield $\mathscr{P}^{(1)}F(x) = (\frac{1}{2})[F(x) + F(-x)]$ and $\mathscr{P}^{(2)}F(x) = (\frac{1}{2})[F(x) - F(-x)]$. Clearly these projected functions are, respectively, even and odd under reflection, as required for them to belong to $\Gamma^{(1)}$ and $\Gamma^{(2)}$, respectively. Our other theorems are illustrated by the facts that any function can be expressed as the sum of odd and even parts constructed as above and that any odd function is orthogonal to any even one.

The techniques developed in this section are useful in setting up proper zero-order symmetry orbitals which belong to a given row of a given representation. We shall later prove that, since the Hamiltonian commutes with the entire group of symmetry operators, then it can have matrix elements only between functions of the same representational classification. This leads to a maximum reduction in the size of the secular equations that must be solved.

3-9 Direct-product Groups

It often occurs that the complete symmetry of the system under consideration can be broken up into two or more types such that the operators of one type commute with those of any other. An important example is that in which the two types of operators operate on entirely different coordinates. For example, in H_2O we can permute the two protons, permute the 10 electrons, and rotate the molecule as a whole. One of each of these three types of operations could be carried out in any order with the same final result. A second example is the separation of orbital and spin operators. A third example is the inversion operator and the group of proper rotations.

Although such cases could be treated with no special attention, we can simplify our work considerably by taking advantage of these properties by introducing the concept of *direct-product groups.* If we have two groups of operators, $\mathscr{G}_a = E, A_2, \ldots, A_{h_a}$ and $\mathscr{G}_b = E, B_2, \ldots, B_{h_b}$ such that all of $\mathscr{G}_a$ commute with all of $\mathscr{G}_b$, then

$$\mathscr{G}_a \times \mathscr{G}_b = E, A_2, \ldots, A_{h_a}, B_2, A_2B_2, \ldots, A_{h_a}B_2, \ldots, A_{h_a}B_{h_b}$$

forms a group of h_ah_b elements, assuming that the only common element in the groups is the identity. To check that this is so, we consider the multiplication of two elements

$$A_kB_lA_{k'}B_{l'} = (A_kA_{k'})(B_lB_{l'})$$

since B_l and $A_{k'}$ commute. But the right member is found in the direct-product group defined above since $\mathscr{G}_a$ and $\mathscr{G}_b$ are separately groups closed under multiplication. Therefore $\mathscr{G}_a \times \mathscr{G}_b$ is also closed, as required.

Representations. It is natural to suppose that the direct-product matrices of the irreducible representations of the component groups might form irreducible representations of the direct-product group. This in fact is the case. As described in Appendix A, the direct product of two matrices **A** and **B** is a matrix **A × B** whose elements are all the products of an element of **A** and one of **B**. Each element bears a double set of subscripts. For example, the element obtained from $A_{ij}B_{kl}$ is labeled $(A \times B)_{ik,jl}$, the two initial indices being given before the comma. The fact that these direct-product matrices in fact have the requisite group-multiplication property follows from the commutivity of ordinary matrix multiplication and the direct-product operation. Thus

$$\begin{aligned}\mathbf{\Gamma}^{(a\times b)}(A_kB_l)\mathbf{\Gamma}^{(a\times b)}(A_{k'}B_{l'}) &= [\mathbf{\Gamma}^{(a)}(A_k)\times\mathbf{\Gamma}^{(b)}(B_l)][\mathbf{\Gamma}^{(a)}(A_{k'})\times\mathbf{\Gamma}^{(b)}(B_{l'})]\\ &= [\mathbf{\Gamma}^{(a)}(A_k)\mathbf{\Gamma}^{(a)}(A_{k'})]\times[\mathbf{\Gamma}^{(b)}(B_l)\mathbf{\Gamma}^{(b)}(B_{l'})]\\ &= \mathbf{\Gamma}^{(a)}(A_kA_{k'})\times\mathbf{\Gamma}^{(b)}(B_lB_{l'})\\ &= \mathbf{\Gamma}^{(a\times b)}(A_kA_{k'}B_lB_{l'})\end{aligned}$$

By an application of Schur's lemma it can be shown[1] that the direct product of two *irreducible* representations forms an *irreducible* representation of the direct product group. We now show that we get *all* the irreducible representations of the direct-product group in this way. Let $l_1^a, l_2^a, \ldots$ and $l_1^b, l_2^b, \ldots$ be the dimensionalities of the irreducible representations of $\mathscr{G}_a$ and $\mathscr{G}_b$. By our dimensionality theorem (3-12),

$$\sum_i (l_i^a)^2 = h_a, \quad \text{and} \quad \sum_j (l_j^b)^2 = h_b.$$

By the definition of the direct-product matrices, their dimensionalities will be $l_{ij} = l_i^a l_j^b$. Then applying (3-12) to the product group

$$\begin{aligned}\sum_{i,j} l_{ij}^2 = \sum_{i,j} (l_i^a l_j^b)^2 &= \sum_i (l_i^a)^2 \sum_j (l_j^b)^2\\ &= h_a h_b = h\end{aligned}$$

where h is the order of the direct-product group. Since $\sum_{i,j} l_{ij}^2 = h$, there can be no other irreducible representations than those expressible as direct products. Note that these direct-product representations carry a double set of representation and row labels. This illustrates how extra quantum numbers arise when there are extra independent degrees of freedom characterized by extra commuting symmetry operators.

Class structure and characters. The class structure of the product group is easily obtained from knowledge of the class structure of the component groups since elements from $\mathscr{G}_a$ commute with those of $\mathscr{G}_b$. Therefore, the number of classes is simply the product of the numbers of classes in $\mathscr{G}_a$ and in $\mathscr{G}_b$ in agreement with the number of irreducible representations in the product group.

An important observation is that the character of any direct-product representation is the product of the characters of the component representations. This is proved by simple inspection of the character,

$$\begin{aligned}\chi^{(a\times b)}(A_kB_l) &= \sum_{i,j} \Gamma^{(a\times b)}(A_kB_l)_{ij,ij}\\ &= \sum_{i,j} \Gamma^{(a)}(A_k)_{ii}\Gamma^{(b)}(B_l)_{jj} = [\sum_i \Gamma^{(a)}(A_k)_{ii}][\sum_j \Gamma^{(b)}(B_l)_{jj}]\\ &= \chi^{(a)}(A_k)\chi^{(b)}(B_l)\end{aligned}$$

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[1] Wigner, *op. cit.*, chap. 16.

This allows us to write out the character table of any group which can be expressed as a direct product with knowledge of only the character tables of the smaller groups from which it is composed. Naturally this provides a great practical simplification.

Example. Let us consider the direct-product group composed of the rotation group of the equilateral triangle (called D_3 in standard notation) and the group $\mathscr{S} = (E, \sigma_h)$. In the latter group, σ_h is the operation of reflection in the plane of the triangle. In standard notation, the direct-product group is called D_{3h}. It is the symmetry group for an equilateral triangle of finite thickness, so that we have an additional six inequivalent positions in which the "numbers on the triangle" have been reflected through onto the other surface. There are now 12 group elements, the original 6 from D_3, each multiplied both by the identity and by σ_h. This is what we mean by the notation $D_{3h} = D_3 \times \mathscr{S}$. The elements of D_3 and $\mathscr{S}$ commute because it makes no difference whether the triangle is first rotated and then subjected to reflection in the plane, or vice versa.

The multiplication table of $\mathscr{S}$ is

	E	σ_h
E	E	σ_h
σ_h	σ_h	E

The group is Abelian; so there are two classes and two one-dimensional irreducible representations. Upon denoting the two representations Γ^+ and Γ^- for even and odd, the character table is simply

$\mathscr{S}$	E	σ_h
Γ^+	1	1
Γ^-	1	−1

Multiplying this table by that for D_3 given in Sec. 3-3, we obtain the character table for the product group D_{3h}.

D_{3h}	E	(A, B, C)	(D, F)	σ_h	$\sigma_h(A, B, C)$	$\sigma_h(D, F)$
$\Gamma^{(1+)}$	1	1	1	1	1	1
$\Gamma^{(2+)}$	1	−1	1	1	−1	1
$\Gamma^{(3+)}$	2	0	−1	2	0	−1
$\Gamma^{(1-)}$	1	1	1	−1	−1	−1
$\Gamma^{(2-)}$	1	−1	1	−1	1	−1
$\Gamma^{(3-)}$	2	0	−1	−2	0	1

For clarity, we have labeled the columns by giving the actual group elements in the class rather than using arbitrary class labels $\mathscr{C}_1, \ldots, \mathscr{C}_6$. Now that the table is worked out, we could dispense completely with the observation that the group D_{3h} may be viewed as a direct product and simply treat it as an ordinary group of order 12. However, the distinction is very worthwhile in reducing the effort required to work out the table. We note in passing that going from D_3 to D_{3h} has not changed the degeneracies (one or two) which are possible in view of the dimensionalities of the irreducible representations. This verifies the assertion made in the example treated at the end of Sec. 3-6.

3-10 Direct-product Representations within a Group

A distinct, although related, example of the use of the direct product is in the formation of a new representation Γ of a given group from two representations $\Gamma^{(1)}$ and $\Gamma^{(2)}$ of the same group. This is done by using as basis functions all possible products of the basis functions from the two initial representations. Let the two bases be

$$\varphi_1, \ldots, \varphi_n \qquad \text{and} \qquad \psi_1, \ldots, \psi_m$$

where n and m are the dimensionalities of $\Gamma^{(1)}$ and $\Gamma^{(2)}$, respectively. Then the functions $\varphi_\kappa \psi_\lambda$ form a basis for an nm-dimensional representation Γ. This may be verified by considering the effect of a transformation operator,

$$\begin{aligned} P_R(\varphi_\kappa \psi_\lambda) &= \sum_{\kappa'} \varphi_{\kappa'} \Gamma^{(1)}(R)_{\kappa'\kappa} \sum_{\lambda'} \psi_{\lambda'} \Gamma^{(2)}(R)_{\lambda'\lambda} \\ &= \sum_{\kappa',\lambda'} \varphi_{\kappa'} \psi_{\lambda'} [\Gamma^{(1)}(R)_{\kappa'\kappa} \Gamma^{(2)}(R)_{\lambda'\lambda}] \\ &= \sum_{\kappa',\lambda'} \varphi_{\kappa'} \psi_{\lambda'} \Gamma(R)_{\kappa'\lambda',\kappa\lambda} \end{aligned}$$

where $\mathbf{\Gamma}(R) = \mathbf{\Gamma}^{(1)}(R) \times \mathbf{\Gamma}^{(2)}(R)$. Thus the direct-product matrices $\mathbf{\Gamma}(R)$ form a representation of the group based on the functions $\varphi_\kappa \psi_\lambda$.

As in the previous section, the character is obtained by taking the product of the characters of the component representations. That is,

$$\chi(R) = \chi^{(1)}(R) \chi^{(2)}(R)$$

where χ is the character for the representation Γ.

An important difference between these direct-product representations and those treated in the previous section is that in the present case the representations are in general reducible. This is obviously true, in view of the limited total number of distinct *irreducible* representations for any given group. If one then forms a new nm-dimensional representation, it must in general be reducible to a sum of irreducible representations. We express this schematically by writing

$$\Gamma^{(i)} \times \Gamma^{(j)} = \sum_k a_{ijk}\Gamma^{(k)} \tag{3-39}$$

As before, this notation means that, if $\mathbf{\Gamma}^{(i)}(R) \times \mathbf{\Gamma}^{(j)}(R)$ is brought to block form, $\mathbf{\Gamma}^{(k)}(R)$ appears a_{ijk} times along the diagonal. We may find the coefficients a_{ijk} by using our standard formula (3-20) for the decomposition of a reducible representation. Since

$$\chi(R) = \chi^{(i)}(R)\chi^{(j)}(R) = \sum_k a_{ijk}\chi^{(k)}(R)$$

$$\begin{aligned} a_{ijk} &= h^{-1} \sum_R \chi^{(i)}(R)\chi^{(j)}(R)\chi^{(k)}(R)^* \\ &= h^{-1} \sum_l N_l\chi^{(i)}(\mathscr{C}_l)\chi^{(j)}(\mathscr{C}_l)\chi^{(k)}(\mathscr{C}_l)^* \end{aligned} \qquad \blacktriangleright \text{(3-40)}$$

Note that if, as is usual, the $\chi^{(k)}(\mathscr{C}_l)$ are real, then a_{ijk} is independent of the order of the indices.

This technique of decomposing a direct-product representation will prove of great usefulness in determining selection rules and in other applications.

EXERCISES

3-1 (*a*) How many inequivalent irreducible representations of D_4, the symmetry group of the square considered in Exercise 2-1, exist? What are their dimensionalities?

(*b*) Work out the character table of this group by inspection, using the rules given in Sec. 3-4. Verify the formula based on the c_{ijk} in several instances.

3-2 Show in general that $\sum_R \chi^{(j)}(R) = 0$ for all representations except the identical representation $\Gamma^{(1)}$, in which all elements are represented by 1. What is the value of the sum for $\Gamma^{(1)}$?

3-3 Write out the matrices of the regular representation of the group D_4 for the elements E, F, G, H. Using these matrices, verify by direct matrix multiplication that $FG = H$.

3-4 Using the regular representation, prove that

$$\sum_j l_j\chi^{(j)}(R) = h$$

if $R = E$ and is zero otherwise. In this l_j is the dimensionality of the jth representation. This result is an additional aid in working out the character tables.

3-5 Work out the orthogonal transformation matrices $R_x(\theta_x)$, $R_y(\theta_y)$, and $R_z(\theta_z)$ for rotations of axes by angles θ_x, θ_y, θ_z about the x, y, z axes, respectively. Take the sense of rotation so that the y axis is rotated toward x in R_z, etc. Using them, compute the matrices $R_x(\theta_x)R_y(\theta_y)$ and $R_y(\theta_y)R_x(\theta_x)$. Note that these rotations do not commute. What is the matrix for $R_xR_y - R_yR_x$? Show that this matrix vanishes as θ^2 if $\theta_x = \theta_y = \theta$ is much less than 1 and corresponds to the *change* $(R_z - E)$ produced by a rotation through θ^2 about the z axis.

3-6 (*a*) Find the transformed functions $P_R f$, $P_S f$, $P_S(P_R f)$, $P_{SR} f$, and $P_{RS} f$, where $f = x$, $R = R_y(\theta_y)$, and $S = R_z(\theta_z)$. Note that $\mathbf{R}^{-1} = \mathbf{R}^{\dagger} = \tilde{\mathbf{R}}$. Generalizing from your results, you may observe that the three p-like functions x, y, z form a basis for a three-dimensional representation of the complete rotation group since

$$P_R p_i = \sum_j p_j \Gamma(R)_{ji}$$

where $i, j = x, y, z$ and R represents any arbitrary rotation. This property is true of the $(2l + 1)$ polynomials equivalent to the spherical harmonics corresponding to any l and of the spherical harmonics themselves.

(*b*) Repeat (*a*) for $f = xy$. Find a convenient set of partners to xy in a basis for representing an arbitrary rotation.

3-7 (*a*) Form a representation of D_3, the rotational symmetry group of the equilateral triangle, which has $F = x^2 z g(r)$ as part of its basis. The z axis is the three-fold axis, and $g(r)$ is such as to assure radial convergence in the normalization integral. What are the other basis functions?

(*b*) If this representation is reducible, into what irreducible representations does it reduce?

(*c*) If your basis functions are not orthonormal, choose a new set of linear combinations of them that are. (You need orthonormalize only the angular part.) By applying the corresponding similarity transformation to the matrices of your representation, transform it into a unitary representation. If you have chosen your orthonormal functions wisely, the matrices will now be in block form. If not, reduce them to block form by a suitable unitary transformation to a new orthonormal basis.

(*d*) Express $F = x^2 z g(r)$ explicitly as a sum of parts $\sum_{j,\kappa} f_\kappa^{(j)}$, each of which transforms according to a particular row of one of the irreducible representations.

3-8 Write out the character table of D_{4h}, taking advantage of the fact that $D_{4h} = D_4 \times i$, where i is the group containing only the inversion and the identity.

3-9 (*a*) Find unitary matrices for all the irreducible representations of D_4. (HINT: Consider the transformation properties of the coordinates x and y in the plane of the square.)

(*b*) How could you now obtain matrices for all the irreducible representations of D_{4h}?

3-10 Work out all direct products $\Gamma^{(i)} \times \Gamma^{(j)} = \sum_k a_{ijk}\Gamma^{(k)}$ of the irreducible representations of the group D_3. Note that a_{ijk} is independent of the subscript order since all the characters involved are real.

3-11 Repeat Exercise 3-10 for the groups D_4 and O, O being the octahedral group discussed in Sec. 4-6, where a character table is given.

REFERENCES

EYRING, H., J. WALTER, and G. E. KIMBALL: "Quantum Chemistry," chap. 10, John Wiley & Sons, Inc., New York, 1944.

HAMERMESH, M.: "Group Theory," Addison-Wesley Publishing Company, Inc., Reading, Mass., 1962.

HEINE, V.: "Group Theory in Quantum Mechanics," Pergamon Press, New York, 1960.

MURNAGHAN, F. D.: "The Theory of Group Representations," chaps. 1–3, The Johns Hopkins Press, Baltimore, 1938.

SPEISER, A.: "Die Theorie der Gruppen von Endlicher Ordnung," chaps. 11–13, 3d ed., Springer-Verlag OHG, Berlin, 1937; reprinted by Dover Publications, Inc., New York, 1945.

VAN DER WAERDEN, B. L.: "Die Gruppentheoretische Methode in der Quantenmechanik," Springer-Verlag OHG, Berlin, 1932.

WEYL, H.: "Gruppentheorie und Quantenmechanik," S. Hirzel Verlag, Leipzig, 1928; translated version, "Theory of Groups and Quantum Mechanics," Dover Publications, Inc., New York, 1950.

WIGNER, E.: "Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren," chaps. 9, 11, 12, and 16, Friedr. Vieweg & Sohn, Brunswick, Germany, 1931; reprinted by J. W. Edwards, Publisher, Incorporated, Ann Arbor, Mich., 1944; revised and translated edition, "Group Theory," Academic Press Inc., New York, 1959.

4 PHYSICAL APPLICATIONS OF GROUP THEORY

In this chapter we shall give a number of illustrative applications of group theory to physical problems. We start by discussing the crystallographic point groups, which play a central role in the theory of molecules and crystalline solids. Then, after a brief introduction to the full rotation group, which is the symmetry group of an isolated atom, we consider the lifting of the orientational degeneracy of the free atom when it is placed into a crystalline environment. This topic, first treated by Bethe in a classic paper, serves as an excellent illustration of the use of the theory of group representations and especially of group characters in physical problems. It also serves as a foundation for the theory of energy bands in solids, which we shall treat in a later chapter. With this crystal-field-splitting example completed, we continue by proving some group-theoretical theorems about matrix elements which determine selection rules. We conclude the chapter with an illustration of the use of group theory in the theory of directed-valence orbitals of specified symmetry.

4-1 Crystal-symmetry Operators

A crystalline solid is a regular array of identical unit cells such that (with edge effects neglected) the crystal is invariant under lattice translations by $\mathbf{T} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$, where n_1, n_2, and n_3 are integers and $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are the primitive translations which define a unit cell. These translations are, however, in general not the only covering operations of the crystal. There are also covering operations, such as rotations, which can be carried out by holding a point (called the origin) fixed. The complete set of covering operations is called the *space group* of the crystal. The group of operations which is obtained by setting all translations in the space-group elements equal to zero is called the *point group* of the crystal. It has been shown[1] that there are only 32 point groups consistent with translational symmetry and that there is a total of 230 possible space groups in all. In a molecule there is no requirement of translational symmetry, and so there is no limit on the number of possible point groups. In practice, though, the most frequently met molecular point groups are among the 32 crystallographic ones. Hence, if we become familiar with them, we are well prepared for the symmetry of molecular as well as crystalline structures.

The fundamental covering operations of which we build up the point groups are the following:

1. Rotations about axes through the origin
2. Reflections in planes containing the origin
3. The inversion, which takes $\mathbf{r}$ into $-\mathbf{r}$

The inversion operator is actually equivalent to a rotation by π followed by reflection in a plane perpendicular to the axis of rotation. However, it enters so frequently that we list it as one of our fundamental operations. In fact, many workers take the inversion as a fundamental operation and the reflections as derived.

Successive operations. For working out the group multiplication properties of these operations it is worth noting the results of various successive operations which frequently occur.

1. The product of two rotations is again a rotation.

2. The product of two reflections is a rotation by an angle $2\varphi_{AB}$ around the line of intersection of the reflection planes A and B, where φ_{AB} is the angle between the planes. For example, in Fig. 4-1*a*, the angle φ_{13} between the initial and final positions is $2\alpha + 2\beta$, which is twice the angle $\varphi_{AB} = (\alpha + \beta)$.

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[1] F. Seitz, *Z. Krist.*, **88**, 433 (1934); **90**, 289 (1935); **91**, 336 (1935); **94**, 100 (1936).

3. The product of a rotation and a reflection in a plane A containing the axis of rotation O is a reflection in another plane B passing through the axis. The angle between the planes is half the angle of rotation, as may be seen in Fig. 4-1*b*.

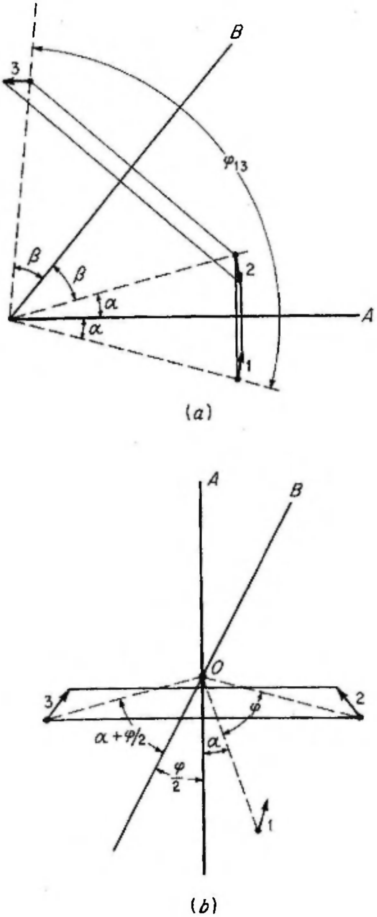
B
3
φ_{13}
β
β
2
α
α
A
1
(a)
A
B
O
3
2
φ
$\alpha+\varphi/2$
α
$\frac{\varphi}{2}$
1
(b)

Fig. 4-1. (*a*) *Diagram illustrating how two reflections produce a rotation;* (*b*) *diagram illustrating how rotation and reflection produce a reflection.*

4. The product of two rotations by π about intersecting axes u and v is a rotation about an axis perpendicular to u and v, the angle of rotation being twice the angle between u and v. This can be illustrated by a diagram quite similar to Fig. 4-1*a*.

Commuting operations. Because of the special group-theoretical and quantum-mechanical significance of commuting operations, it is worth noting that the following pairs of operations commute:

1. Two rotations about the same axis.
2. Two reflections in perpendicular planes.
3. Two rotations by π about perpendicular axes.
4. A rotation and a reflection in a plane perpendicular to the axis of rotation. The resulting combination is called an *improper rotation*, or a *rotary reflection*. An improper rotation by π is identical with the inversion operation.
5. The inversion and any rotation or reflection.

Notation. We now list the standard Schoenflies notation for the various types of symmetry operations which can occur in the crystallographic point groups.

E = identity.
C_n — rotation through $2\pi/n$. We shall show that in solids n can take on only the values 1, 2, 3, 4, and 6.
σ = reflection in a plane.
σ_h = reflection in the "horizontal" plane, i.e., the plane through the origin perpendicular to the axis of highest rotation symmetry.
σ_v = reflection in a "vertical" place, i.e., one passing through the axis of highest symmetry.
σ_d = reflection in a "diagonal" plane, i.e., one containing the symmetry axis and bisecting the angle between the twofold axes perpendicular to the symmetry axis. This is just a special kind of σ_v.
S_n — improper rotation through $2\pi/n$.
$i = S_2$ = inversion.

Interrelations of symmetry elements. As a final list of general observations concerning these symmetry elements, we now give some necessary interrelations of symmetry elements. These observations help to reduce the amount of information which is needed to determine the complete symmetry of the problem. The verification of the rules may be carried out by elementary geometrical considerations. We list the following rules:

1a. The intersection of two reflection planes must be a symmetry axis. If the angle φ between the planes is π/n, the axis is n-fold.

1b. If a reflection plane contains an n-fold axis, there must be $n - 1$ other reflection planes at angles of π/n.

2a. Two twofold axes separated by an angle of π/n require a perpendicular n-fold axis.

2b. A twofold axis and an n-fold axis perpendicular to it require $n - 1$ additional twofold axes separated by angles of π/n.

3. An even-fold axis, a reflection plane perpendicular to it, and an inversion center are interdependent. Any two of these elements implies the existence of the third.

4-2 The Crystallographic Point Groups

Having collected a large number of the general properties of the sort of symmetry operations which comprise the point groups, we now proceed to enumerate and describe the 32 point groups which exhaust the possible symmetries of a crystal. These groups fall into two general categories—the simple rotation groups and the groups of higher symmetry. In the former, there is one symmetry axis (called Z) of higher symmetry than any other. In the latter, there is no unique axis of highest symmetry, but more than one n-fold axis, where $n > 2$. While we are at it, we also include a third type of point group, namely, groups containing C_∞. These groups form the point groups of linear molecules but are inconsistent with the translational symmetry required for crystalline solids.

We begin our enumeration with the simple rotation groups. These groups are easily visualized by means of *stereographic projections.* To form these, we project onto the XY plane the position of a mark at a general point on a unit sphere which is subjected to the various symmetry operations of the group. If the mark is above the plane, we use a $+$; if below, a $\circ$. The rotation axes are indicated by characteristic symbols. The projections of all 27 crystallographic point groups of the simple rotation type are collected in Fig. 4-2. We now proceed to consider the various possibilities. We follow the Schoenflies system of notation, in which the groups are labeled in a way which suggests the independent group elements required to determine all the elements of the group.

C_n ■ These are the point groups in which the only symmetry consists of a single n-fold axis of symmetry. These groups are cyclic Abelian groups of order n. The group C_6, for example, contains C_6, $(C_6)^2 = C_3$, $(C_6)^3 = C_2$, $(C_6)^4 = (C_3)^{-1}$, $(C_6)^5 = (C_6)^{-1}$, $(C_6)^6 = E$.

We now prove that the only cases consistent with the translational symmetry of a crystalline solid are C_1, C_2, C_3, C_4, and C_6. The proof is based on the existence of a translation of minimum length which is perpendicular to the rotation axis. Such perpendicular translational symmetry elements must exist in the space group of any crystal, because one may construct them from *any* translational symmetry element

$$\mathbf{T} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3.$$

This is done by rotating $\mathbf{T}$ about the rotational axis to a new position $\mathbf{T}'$ and then taking $\mathbf{T} - \mathbf{T}'$, which must also be a translational-symmetry element. We then may select the shortest of these perpendicular translations and call it $\mathbf{R}$. Now applying C_n to $\mathbf{R}$ yields another allowed translation $\mathbf{R}'$ of the same magnitude as $\mathbf{R}$, but rotated through $2\pi/n$. But $\mathbf{R} - \mathbf{R}'$ must also be an allowed translation, since the translation group is closed under

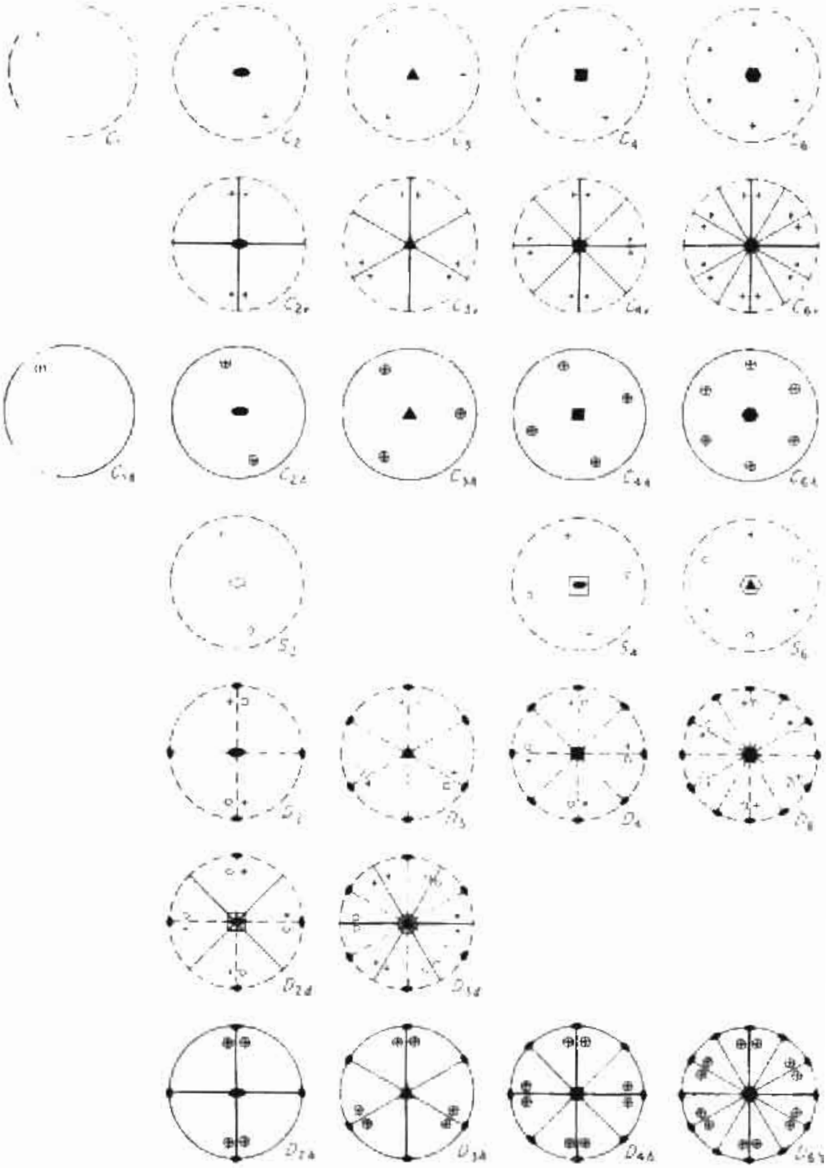
C_1
C_2
C_3
C_4
C_6
C_{2v}
C_{3v}
C_{4v}
C_{6v}
C_{1h}
C_{2h}
C_{3h}
C_{4h}
C_{6h}
S_2
S_4
S_6
D_2
D_3
D_4
D_6
D_{2d}
D_{3d}
D_{2h}
D_{3h}
D_{4h}
D_{6h}

Fig. 4-2. *Stereographic projections of simple point groups.*

vector addition. The length of $\mathbf{R} - \mathbf{R}'$ is $2\,|R| \sin(\pi/n)$, as is clear from Fig. 4-3*a*. Since **R** is by definition the smallest translation, we have

$$2\,|R| \sin \pi/n \geq |R|$$

or

$$n \leqq 6$$

Thus all rotation axes greater than sixfold are impossible in crystals. By a similar argument, $n = 5$ is specifically excluded because it would give

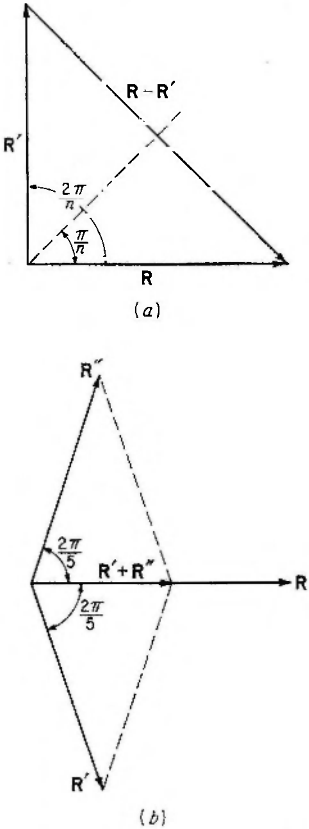

Fig. 4-3. *Diagrams illustrating generation of translations perpendicular to an n-fold rotation axis.* (*a*) $n = 4$, $|\mathbf{R}\text{-}\mathbf{R}'| > |\mathbf{R}|$; (*b*) $n = 5$, $|\mathbf{R}' + \mathbf{R}''| < |R|$.

$|\mathbf{R}' + \mathbf{R}''| < |\mathbf{R}|$ for the rotations shown in Fig. 4-3*b*. Thus the requirement of translation symmetry with a discrete unit cell restricts the possible rotation axes in crystals to $n = 1, 2, 3, 4, 6$.

C_{nv} ■ These groups contain a σ_v reflection plane in addition to th C_n axis. By rule 1*b* at the end of the previous section, this implies th existence of n reflection planes, separated by an angle of π/n around the C

axis. Solid radial lines on the stereographic projections indicate the vertical reflection planes.

C_{nh} ■ These groups contain a σ_h reflection as well as the C_n axis. The reflection plane is indicated on the stereographic projection by making the unit circle solid rather than broken. Reflection in this plane takes + into ○. Note that all groups of the sort $C_{2n,h}$ automatically include the inversion element i.

S_n ■ These groups contain an n-fold axis for improper rotations. If n is odd, these groups are identical with C_{nh} and hence they are not considered. If n is even, they form distinct groups, each of which includes $C_{n/2}$ as a subgroup. The cases occurring in crystals are thus S_2, which is equivalent to simple inversion symmetry, S_4, and S_6, which may be considered as the direct-product group $C_3 \times i$. The axes of improper rotations are shown on stereographic projections as hollow figures.

D_n ■ These groups have n twofold axes perpendicular to the principal C_n axis. In D_2, therefore, there are three mutually perpendicular twofold axes. The group D_2 is sometimes called V for the German *Vierergruppe*, mentioned previously in Sec. 2-6.

D_{nd} ■ These groups contain the elements of D_n together with diagonal reflection planes σ_d bisecting the angles between the twofold axes perpendicular to the principal rotation axis.

D_{nh} ■ These groups contain the elements of D_n plus the horizontal reflection plane σ_h. Hence, D_{nh} has twice as many elements as D_n.

In working out character tables and in other applications, it is useful to note that some of the above-mentioned groups are conveniently expressed as direct products of simpler groups with the group of the inversion. These are

$$\begin{aligned} C_{2h} &= C_2 \times i & \qquad D_{2h} &= D_2 \times i \\ C_{4h} &= C_4 \times i & \qquad D_{4h} &= D_4 \times i \\ C_{6h} &= C_6 \times i & \qquad D_{6h} &= D_6 \times i \\ S_6 &= C_3 \times i & \qquad D_{3d} &= D_3 \times i \end{aligned} \tag{4-1}$$

We now proceed to consider the groups of higher symmetry. The five groups in this category—T, T_d, T_h, O, O_h—have no unique axis of highest symmetry but rather have more than one axis which is at least of threefold symmetry. In order to make all these rotation axes consistent with translational crystal symmetry, the crystal must belong to the *cubic* crystal system, in which the fundamental translational vectors are mutually perpendicular and of equal length. Accordingly, it will be convenient to consider all these groups in conjunction with a unit cube.

T ■ This is the smallest of the groups of higher symmetry. It consists of the 12 proper rotational operations which take a regular tetrahedron into itself. These operations can be readily visualized if we consider the tetrahedron *abcd* inscribed in a cube as shown in Fig. 4-4. The X, Y, and Z axes are normal to cube faces, and the origin is at the center of the cube. The covering operations of the tetrahedron are then seen to be E; three C_2's about the X, Y, and Z axes, respectively; and eight C_3's about the body diagonals of the cube. The latter actually comprise two distinct classes of four elements each. These classes may be considered to be, respectively, the clockwise and counterclockwise rotations by $2\pi/3$ about the four threefold axes leaving the tetrahedron normally at the center of the faces. Despite the fact that all these are threefold rotations about face-center axes, these two types of operations form distinct classes because these threefold axes are "directed." That is, there is no operation in the group (such as a perpendicular twofold axis) which will reverse the line of the axis.

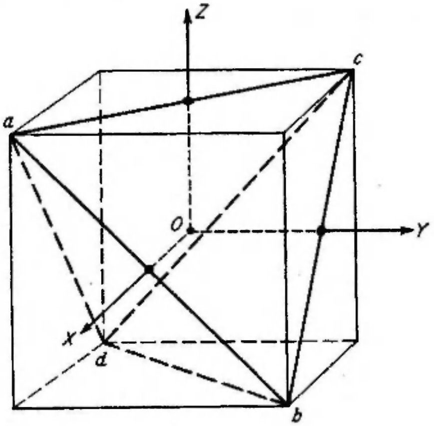

Fig. 4-4. *Tetrahedron inscribed in cube.*

T_d ■ The full tetrahedral group T_d contains all the covering operations of a regular tetrahedron, including reflections. It is the symmetry group of CH_4, for example. Upon applying the theorem proved in Sec. 2-5, the fact that T is a subgroup of T_d implies that the order of T_d must be an integral multiple of 12, the order of T. In fact T_d has 24 elements. Six of the extra elements are diagonal reflection planes normal to a cube face and passing through a tetrahedral edge such as *ac* or *ab*. The existence of these six σ_d's implies the existence of six S_4's about the (positive and negative) X, Y, and Z directions. This completes the group. Note that the reflection planes in T_d allow one to interchange clockwise and counterclockwise rotations. Hence, unlike the situation in T, all eight C_3's are in the same class in the group T_d.

T_h ■ We can form another group of order 24 based on T by taking the direct product of T with the group of the inversion operator. The nature of all its elements follows from this description. Note that a regular tetrahedron does *not* have the symmetry T_h since it has no inversion symmetry.

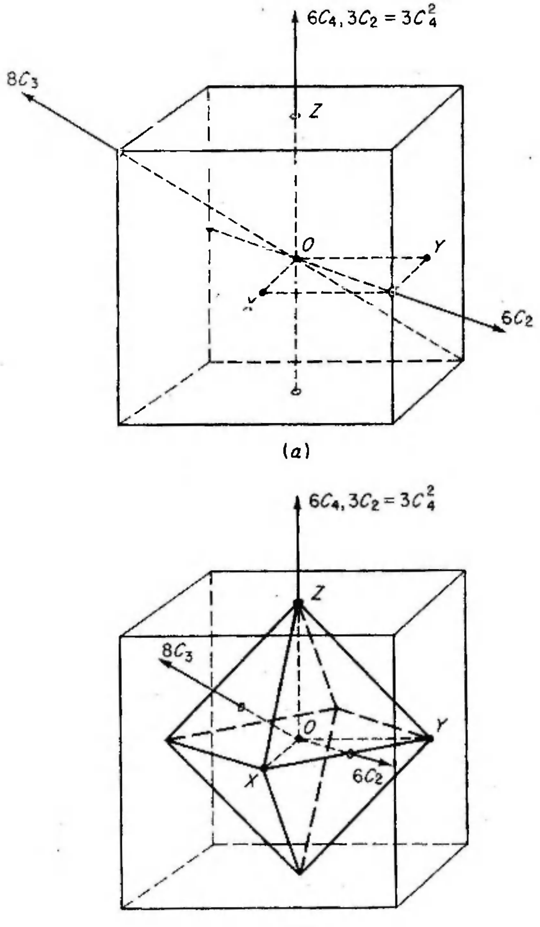

Fig. 4-5. (*a*) *Rotational symmetries of a cube;* (*b*) *rotational symmetries of a regular octahedron.*

O ■ One of the most important of all the point groups is the octahedral group O, the group of proper rotations which take a cube or an octahedron into itself. This group contains the following 24 elements: E; eight C_3's about cube body diagonals; three C_2's about the X, Y, Z axes; six C_4's about the X, Y, Z axes; and six C_2's about axes through the origin parallel to face diagonals. Note that all the C_3's are in the same class since a counterclockwise rotation about a given corner is clockwise about the diametrically opposite corner, which may be exchanged with it by one of the twofold rotations from the group. Clearly the two types of C_2 operations mentioned are not physically equivalent, and hence they form separate classes. We have described the symmetry operations for a cube. The corresponding octahedron with the same symmetry elements has a vertex at the face centers of the cube and a face center corresponding to each cube corner. Typical elements for these symmetries are indicated in Fig. 4-5.

O_h ■ The full octahedral group $O_h = O \times i$ is the largest of all the point groups, evidently containing 48 elements. It is the full symmetry group of a cube or octahedron, including improper rotations and reflections.

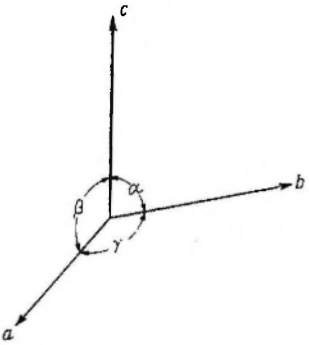

Fig. 4-6. *Labeling of unit-cell parameters.*

The existence of 48 elements implies that a general point may be mapped into 48 distinct equivalent points by successive application of the symmetry operations of the group.

We conclude our enumeration by describing two groups containing C_∞ which occur in linear molecules.

$C_{\infty v}$ ■ This is the group of a general linear molecule. It has full rotational symmetry about the molecular axis and reflection symmetry in any (vertical) plane passing through the axis.

$D_{\infty h}$ ■ This group contains a horizontal reflection plane and twofold symmetry about any axis in this plane passing through the molecular center. These symmetries imply in addition the existence of inversion symmetry and vertical reflection planes. $D_{\infty h}$ is the symmetry group of a homonuclear diatomic molecule or a symmetric linear molecule of the *ABA* type, such as CO_2.

Crystal systems. For applications it is convenient to tabulate the 32 crystallographic point groups according to the crystal system to which they belong. That is, we give the properties of the translational unit cell which are required for compatibility with the point-group symmetry. The unit cell is specified by the three translations a, b, c and three angles α, β, γ as shown in Fig. 4-6. In Table 4-1, we also list the number of elements in each point group.

Table 4-1

Classification of the point groups according to crystal systems

System	*Unit cell*	*Groups*	*Number of symmetry elements*
Triclinic	$a \neq b \neq c$	C_1	1
	$\alpha \neq \beta \neq \gamma$	$S_2(C_i)$	2
Monoclinic	$a \neq b \neq c$	C_{1h}	2
	$\alpha = \gamma = \pi/2 \neq \beta$	C_2	2
		C_{2h}	4
Orthorhombic	$a \neq b \neq c$	C_{2v}	4
	$\alpha = \beta = \gamma = \pi/2$	$D_2(V)$	4
		$D_{2h}(V_h)$	8
Tetragonal	$a = b \neq c$	C_4	4
	$\alpha = \beta = \gamma = \pi/2$	S_4	4
		C_{4h}	8
		$D_{2d}(V_d)$	8
		C_{4v}	8
		D_4	8
		D_{4h}	16
Rhombohedral (trigonal)	$a = b = c$	C_3	3
	$\alpha = \beta = \gamma < 2\pi/3 \neq \pi/2$	$S_6(C_{3i})$	6
		C_{3v}	6
		D_3	6
		D_{3d}	12
Hexagonal	$a = b \neq c$	C_{3h}	6
	$\alpha = \beta = \pi/2, \gamma = 2\pi/3$	C_6	6
		C_{6h}	12
		D_{3h}	12
		C_{6v}	12
		D_6	12
		D_{6h}	24
Cubic	$a = b = c$	T	12
	$\alpha = \beta = \gamma = \pi/2$	T_h	24
		T_d	24
		O	24
		O_h	48

4-3 Irreducible Representations of the Point Groups

Given the number of elements in each point group and its class structure, the number and dimensionality of its irreducible representations are fixed by the rules set down in Sec. 3-4. Moreover, we can also work out the complete character tables by the methods cited there. This has been done, and the results are tabulated in various references such as the books of Margenau and Murphy and of Eyring, Walter, and Kimball. For convenience we reproduce these results in Appendix B. Not all 32 groups are tabulated separately since some are direct products of simpler groups with the group of the inversion. It will also be noted that a number of sets of isomorphous groups have been included individually. This has been done to reduce the confusion of multiple labeling in the tables.

As an example, consider the table for our standard example group D_3. As given in the Appendix, the character table is:

D_3			E	$2C_3$	$3C_2'$
$x^2 + y^2, z^2$		A_1	1	1	1
	R_z, z	A_2	1	1	-1
(xz, yz) $(x^2 - y^2, xy)$	(x, y) (R_x, R_y)	E	2	-1	0

The columns are labeled according to the number and type of operations forming each class. In particular, C_2' refers to a twofold axis perpendicular to the principal threefold axis. Had there been other inequivalent twofold axes, they would have been labeled C_2''. The labels of the irreducible representations are A or B for one-dimensional representations. Those having a character $+1$ under the principal rotation C_n are labeled A; those with -1 are labeled B. Two-dimensional representations are labeled E, and three-dimensional ones are labeled T. When inversion symmetry is present, it is customary to use g and u as subscripts for even and odd (*gerade* and *ungerade*), respectively.

The other columns list the coordinates, quadratic forms of coordinates, and rotations R_x, R_y, R_z about the coordinate axes to indicate the representation according to which they transform. These assignments can be checked by use of the projection operators $\mathscr{P}^{(j)}$ introduced in Sec. 3-8 or by more elementary inspection procedures.

Classification of functions by transformation properties. Let us consider some explicit examples of this important concept of classifying functions or operators as belonging to some particular irreducible representation. The simplest case arises in a group having only one-dimensional representations, since then the characters actually are the complete representation matrices.

Consider, for example, the group C_{2v}. Its character table is:

C_{2v}			E	C_2	σ_v	σ_v'
x^2, y^2, z^2	z	A_1	1	1	1	1
xy	R_z	A_2	1	1	−1	−1
xz	R_y, x	B_1	1	−1	1	−1
yz	R_x, y	B_2	1	−1	−1	1

Our notation here is such that σ_v is reflection in the xz plane and σ_v' is reflection in the yz plane. Then we can write out symbolically the effect of each of these operations (or its inverse, which is the same in this example) on the three coordinate functions as follows:

$$P_E\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}x\\y\\z\end{pmatrix}\quad P_{C_2}\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}-x\\-y\\z\end{pmatrix}\quad P_{\sigma_v}\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}x\\-y\\z\end{pmatrix}\quad P_{\sigma_v'}\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}-x\\y\\z\end{pmatrix}$$

Comparing the results with the character table, and using the fact that $\chi^{(i)}(R) = \Gamma^{(i)}(R)$ for a one-dimensional representation, we have, for example,

$$P_{C_2}x = \Gamma^{(B_1)}(C_2)x$$

or more generally $$P_R x = \Gamma^{(B_1)}(R)x$$

Similarly, $$P_R y = \Gamma^{(B_2)}(R)y$$

and $$P_R z = \Gamma^{(A_1)}(R)z$$

We summarize these results by saying that, under the group C_{2v}, x transforms according to B_1, y according to B_2, and z according to A_1. From these results it follows that xy transforms according to $B_1 \times B_2 = A_2$, etc.

The confirmation of assignments by the projection operator technique may be illustrated by letting $\mathscr{P}^{(A_2)}$ operate on xy. This gives

$$\begin{aligned}\mathscr{P}^{(A_2)}xy &= \frac{l_{A_2}}{h}\sum_R \chi^{(A_2)}(R)P_R xy\\ &= \tfrac{1}{4}\{xy + (-x)(-y) - x(-y) - (-x)y\}\\ &= xy\end{aligned}$$

Thus xy does indeed belong to A_2.

To illustrate the situation which arises with representations of higher order, we now consider our standard example D_3. We take the z axis as the threefold axis, the x axis as the A rotation axis (see Fig. 2-1), and the y axis as the axis perpendicular to both of these. Now, if we apply operators to the simple functions x, y, z, we can work out a matrix representation.

For example,

$$P_E\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}x\\y\\z\end{pmatrix}\qquad P_D\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}-\dfrac{x}{2}+\dfrac{\sqrt{3}y}{2}\\ -\dfrac{\sqrt{3}x}{2}-\dfrac{y}{2}\\ z\end{pmatrix}\qquad P_A\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}x\\-y\\-z\end{pmatrix}$$

Note that in working out the effect of P_D we must be careful of the sense of the 120° rotation because $D \neq D^{-1}$. Thus $P_D f(\mathbf{x}) = f(\mathbf{D}^{-1}\mathbf{x})$; or, in words, we rotate the coordinates counterclockwise to represent a clockwise rotation of the object.

If we write out the result of all six operations of the group in this way, we note that z always transforms only into a multiple of itself. Hence z alone forms a basis for a one-dimensional representation of the group. Since the character under A is seen to be -1, $\chi(C_2) = -1$ and the representation is identified as A_2 by reference to the character table. With x and y the situation is more complicated since cross terms occur under the operation D. Hence x and y together form a basis for a two-dimensional representation which is readily seen to be irreducible and hence must be E. The matrices can be obtained by inspecting the results above, and they are found to coincide with those introduced in defining the group originally in Sec. 2-2. Again care is required to keep the indices straight. For example, labeling the rows by x, y,

$$P_D x = x\Gamma(D)_{xx} + y\Gamma(D)_{yx}$$

Thus, $\Gamma(D)_{xx} = -\frac{1}{2}$ and $\Gamma(D)_{yx} = -\sqrt{3}/2$, and $\mathbf{\Gamma}(D)$ coincides with the matrix D introduced earlier. This agreement is by no means accidental. Because only one two-dimensional representation of D_3 exists, the matrices found here could at most differ from those given before by a similarity transformation corresponding to the choice of two independent linear combinations of x and y as basis functions. This example illustrates a common and powerful method of finding the matrices of the irreducible representations of some given group.

Although the matrices may be derived by consideration of simple functions like x and y, this in no way means that their applicability is so restricted. There are in general infinitely many pairs of functions which will transform in the same way. For example, since $x^2 + y^2$ and z^2 belong to A_1, the totally symmetric representation, any function $\varphi(x^2 + y^2, z^2)$ is invariant under all operations of D_3. Hence, if we consider $x\varphi$ and $y\varphi$, for any such φ, we have two functions which transform in the same way as x and y. In this way a relatively small number of matrices can describe the transformation properties of *all* possible eigenfunctions for a given problem.

4-4 Elementary Representations of the Three-dimensional Rotation Group

In the next section we shall begin to investigate the sorts of eigenfunctions and degeneracies which are consistent with the symmetries experienced by electrons in a crystal. In many cases the perturbing influence of the crystalline environment is small enough to make it worthwhile to consider the free atom or ion as a starting point. In this section we prepare for this application by giving a brief survey of the elementary representations of the group of all rotations in three dimensions, which is the rotational-symmetry group for an atom in free space. These are the odd-dimensional representations corresponding to integral angular momentum, for which the spherical harmonics form convenient sets of basis functions. We shall give a much more detailed treatment of this group in the next chapter.

The set of all rotations in three-dimensional space obviously forms an infinite group—the covering operations of a sphere. There are also an infinite number of classes, all rotations through the same angle (about whatever axis) being in the same class because another rotation of the group connects the two rotation axes. Therefore, there must also be an infinite number of irreducible representations. We can find the representations of odd dimensionality by taking the spherical harmonics

$$Y_l^m(\theta, \varphi) \sim P_l^m(\theta)e^{im\varphi}$$

as basis functions. It is a well-known property of the spherical harmonics that if we shift the polar axis we can express the resulting $Y_l^m(\theta', \varphi')$ in terms of a linear combination of all the $Y_l^{m'}(\theta, \varphi)$ of *the same l*. That is, we can write

$$P_R Y_l^m = \sum_{m'} \Gamma^{(l)}(R)_{m'm} Y_l^{m'} \tag{4-2}$$

[If $m = 0$, the $\Gamma^{(l)}(R)_{m'0}$ can be determined by using the addition theorem for spherical harmonics to be simply $\sim Y_l^{-m'}(\theta'', \varphi'')$, where θ'' and φ'' are the angles giving the direction of the new polar axis.] This means that the $2l + 1$ functions Y_l^m form a basis for a representation of the full rotation group. One might imagine that the representation is irreducible, since all $2l + 1$ functions enter in (4-2), and that is in fact the case. We shall see shortly that these spherical harmonic representations exhaust the possible odd-dimensional representations.

Characters. If we rotate the contours of the function by α about the z axis (or make a rotation of axes by $-\alpha$), the effect upon the spherical harmonic is simple, namely,

$$P_\alpha Y_l^m(\theta, \varphi) = Y_l^m(\theta, \varphi - \alpha) = e^{-im\alpha} Y_l^m(\theta, \varphi) \tag{4-3}$$

Thus the representation of such a rotation is the diagonal matrix

$$\mathbf{\Gamma}^{(l)}(\alpha) = \begin{pmatrix} e^{-il\alpha} & 0 & \cdots & 0 \\ 0 & e^{-i(l-1)\alpha} & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & e^{il\alpha} \end{pmatrix} \tag{4-4}$$

Hence the character is

$$\chi^{(l)}(\alpha) = \operatorname{Tr} \mathbf{\Gamma}^{(l)}(\alpha) = e^{-il\alpha} + \cdots + e^{il\alpha} \tag{4-5}$$

This sum can be carried out explicitly as follows by factoring out a geometric series:

$$\begin{aligned} \chi^{(l)}(\alpha) &= e^{-il\alpha} \sum_{k=0}^{2l} (e^{i\alpha})^k \\ &= e^{-il\alpha} \frac{e^{i(2l+1)\alpha} - 1}{e^{i\alpha} - 1} \\ &= \frac{e^{i(l+\frac{1}{2})\alpha} - e^{-i(l+\frac{1}{2})\alpha}}{e^{i\alpha/2} - e^{-i\alpha/2}} \\ &= \frac{\sin (l + \frac{1}{2})\alpha}{\sin (\alpha/2)} . \end{aligned} \qquad \blacktriangleright \text{(4-6)}$$

We have previously noted that all rotations by α are in the same class, regardless of axis. Hence, they must all have the character calculated here for a simple special case.

Finally, we show that there can be no other inequivalent irreducible representations of odd order. If there were such, they would have to have a character orthogonal to the characters of all those found above. But if they are orthogonal to all of them, they must be also orthogonal to the difference of two successive ones such as $[\chi^{(l)}(\alpha) - \chi^{(l-1)}(\alpha)]$. However, this difference is just $2 \cos l\alpha$. Thus any additional representation would need to have a character $\chi(\alpha)$ orthogonal to a Fourier series of cosines. Since rotations by $\pm\alpha$ are in the same class, χ must be an even function of α. Hence, there is no possibility of any new $\chi(\alpha)$ being orthogonal to a cosine series, and *the spherical harmonics of order l form the basis for the only distinct irreducible representation of dimensionality* $(2l + 1)$ *of the full rotation group.* Its character is given by (4-5) or (4-6) above.

Although this proof may seem so general as to exclude *any* other representations, we shall in fact be led to consider even-dimensional representations, corresponding to half-integral angular momenta. It turns out that the formulas derived above still hold for the characters. Hence the new characters are orthogonal to those of the odd-dimensional representation *if* the domain of α is extended from $\pm\pi$ to $\pm 2\pi$. This curious extension is required because of the double-valued nature of the basis functions of half-integral angular momentum. As we shall show, rotation by 2π produces a sign change, and rotation by 4π serves as the identity. Since all observable quantities depend on bilinear combinations of these functions, no physical anomalies arise from the resulting sign ambiguity.

4-5 Crystal-field Splitting of Atomic Energy Levels

When an atom or ion is located, not in free space, but in a crystal, it is subjected to various inhomogeneous electric fields which destroy the isotropy of free space. Thus the symmetry group is reduced from that of the full three-dimensional rotation group plus the inversion to some finite group of rotations through finite angles and perhaps also reflections. This reduced group allows the originally irreducible representations of the full rotation group based on spherical harmonics (angular-momentum eigenfunctions) to be reduced with respect to this subgroup. This reduction in the dimensionality of the irreducible representations causes the degeneracy associated with complete rotational symmetry to be lifted. Hence the free-ion energy levels are split by the crystalline electric field. As first pointed out by Bethe,[1] the degree of residual degeneracy is determined from the symmetry by group theory with ultimate accuracy since no perturbation-theory approximation is involved. However, to calculate the magnitudes of the splittings or the order of the levels, it is of course necessary to employ more specific knowledge of the crystalline field. Given such knowledge, semiquantitative predictions of the splittings can be made by perturbation methods. In addition to these zero-field splittings, the additional splitting produced by an external magnetic field can be elegantly handled by the use of "spin Hamiltonians." These may be obtained by perturbation theory or simply guessed on the basis of symmetry. The spin-Hamiltonian method is presented in review papers by Bleaney and Stevens and by Bowers and Owen,[2] and it has been extremely successful in describing the results of paramagnetic-resonance experiments. We shall not go into it here, however, as it generally entails a more restricted and specific approach than required by purely group-theoretical considerations.[3]

As mentioned above, the splittings are most accurately studied by microwave paramagnetic resonance. However, they were first studied by means of magnetic-susceptibility and heat-capacity experiments and in optical absorption in solids. The magnitude of the splittings can range from

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[1] H. Bethe, *Ann. Physik*, **3**, 133 (1929).

[2] B. Bleaney and K. W. H. Stevens, *Rept. Progr. Phys.*, **16**, 108 (1953); K. D. Bowers and J. Owen, *ibid.*, **18**, 304 (1955).

[3] G. F. Koster and H. Statz, *Phys. Rev.*, **113**, 445 (1959).

~ 0.01 cm^{-1} up to $\sim 50{,}000$ cm^{-1}, depending on the ion involved and the nature of the crystalline field. This great range makes the use of different methods valuable for handling different cases. We distinguish three cases depending on whether the crystal-field energies are small compared with the spin-orbit coupling (rare-earth ions), large compared with spin-orbit coupling but small compared with term separations (iron group), or large compared even with the term separations (covalent complexes). After some general remarks about the origin of the crystal field, we shall return to treat some of these cases.

Form of the crystal field. In any given crystalline environment, one can estimate the potential near the ion in question by replacing each neighboring ion by a point charge. Taking our origin of coordinates at the center of the magnetic ion, we can then make a Taylor's-series expansion of the resulting potential. An ion of charge e at $x = -a, y = z = 0$ will contribute

$$\begin{aligned} V(x, y, z) &= e[(a + x)^2 + y^2 + z^2]^{-\frac{1}{2}} \\ &= \frac{e}{a}\left(1 - \frac{x}{a} - \frac{r^2}{2a^2} + \frac{3}{2}\frac{x^2}{a^2} + \cdots\right) \end{aligned}$$

Putting another charge at $x = +a$ gives a situation with inversion symmetry, causing all odd powers of x to drop out. If we add four more charges at $\pm a$ on the y and z axes to form a regular octahedron of charges, we get further simplifications. The first term with less than spherical symmetry is

$$V_c = \frac{35}{4}\frac{e}{a^5}(x^4 + y^4 + z^4 - \tfrac{3}{5}r^4) \tag{4-7}$$

which is of course invariant under all the operations of the full octahedral group O_h. This is often referred to as the cubic-field term, as it is the leading nonspherical term in the potential of cubic symmetry. If the symmetry were less complete than this, e.g., if the charges were at $\pm c \neq \pm a$ along the z axis, then nonspherical terms would remain in the second order, as well as higher-order terms.

Note that all these potentials must obey Laplace's equation, since they are being produced by charges outside the region of interest. This restricts their forms to linear combinations of expressions of the sort $r^l Y_l^m(\theta, \varphi)$. For example, if there is axial symmetry about the z axis, the leading term is

$$V_a \sim r^2 Y_2^0(\theta) \sim 3z^2 - r^2 \tag{4-8}$$

If there is only orthorhombic symmetry, the leading term is

$$V_r \sim Ax^2 + By^2 - (A + B)z^2 \tag{4-9}$$

This V_r is a mixture of Y_2^0 and $(Y_2^2 + Y_2^{-2}) \sim (x^2 - y^2)$, both of which are invariant under D_2.

The method of estimation outlined above gives a reasonable estimate of the magnitude of the crystalline field, but it is far from rigorous. Errors arise from overlap, nonspherical charge distributions, and exchange effects.[1] These effects do *not* affect the symmetry properties, however. If x, y, and z are equivalent, they will be equivalent even in the presence of these subtleties and the leading term in the effective potential will still act like V_c. However, in the absence of extremely elaborate calculations, the coefficient will have to be determined experimentally from the magnitude of some splitting which it produces. If we are content with those results which can actually be determined theoretically from rigorous symmetry properties, we need not try to compute potentials and consider perturbation theory at all. We can obtain these results directly by the use of group theory.

4-6 Intermediate Crystal-field-splitting Case

Since more work has been done on iron-group ions than on those of any other sort, we first consider the iron-group case in which the crystal-field splitting is intermediate between the spin-orbit energy and the separation of L-S terms in the free atom. This means that L and S will remain approximately good quantum numbers, but J will not. Since the crystal field acts only on the orbital motion (position) of the electrons, it will split the $(2L + 1)$-fold orbital degeneracy but will affect the spin degeneracy only via the (weak) spin-orbit coupling. Thus we initially ignore spin completely and work out the orbital splittings. Later on we shall show how the spin is to be handled.

We proceed by example. Consider the case of an ion in a crystal at a site where it is surrounded by a regular octahedron of negative ions. This is a reasonable approximation of the real situation in a large number of instances. As noted above, $V_c \sim (x^4 + y^4 + z^4 - 3r^4/5)$ would be the leading term in the potential, but we shall use only the symmetry of the situation. This is described by the group O_h, but for the present we shall consider only the 24 proper rotations comprising the group O. Later (Sec. 4-10) we shall show that inclusion of the inversion to form O_h introduces nothing new. For convenience, the character table of O is reproduced here, including a variety of labels for the various irreducible representations which have been introduced in the literature and are still in use. Those given in the first two columns are used by Bouckaert, Smoluchowski, and Wigner and by Von der Lage and Bethe.[2] Both are systems of notation in which a prime changes the parity or inversion symmetry, and the labels given all refer to the even parity case. The third column is the notation used in Bethe's original paper, and the fourth is the conventional one used in most character tables for molecular applications. Upon recalling the discussion of Sec. 4-2, the $8C_3$'s are rotations about face centers of the octahedron (body diagonals of the complementary cube); the $3C_2$'s and $6C_4$'s are rotations about the corners of the octahedron (face centers of the cube); and the $6C_2$'s are about the remaining symmetry axes through midpoints of edges. These axes are illustrated in Fig. 4-5.

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[1] See, for example, J. C. Phillips, *J. Phys. Chem. Solids*, **11**, 226 (1959); A. J. Freeman and R. E. Watson, *Phys. Rev.*, **120**, 1254 (1960).

[2] L. P. Bouckaert, R. Smoluchowski, and E. P. Wigner, *Phys. Rev.*, **50**, 58 (1936); F. C. Von der Lage and H. Bethe, *Phys. Rev.*, **71**, 612 (1947).

O				E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
Γ_1	α	Γ_1	A_1	1	1	1	1	1
Γ_2	β'	Γ_2	A_2	1	1	1	-1	-1
Γ_{12}	γ	Γ_3	E	2	-1	2	0	0
Γ'_{15}	δ'	Γ_4	T_1	3	0	-1	-1	1
Γ'_{25}	ϵ	Γ_5	T_2	3	0	-1	1	-1

Now consider an atomic term with orbital angular momentum L. The $(2L+1)$ spherical harmonics Y_L^M, which are degenerate in isotropic space, form the basis for a representation which we have called $\Gamma^{(L)}$. We now change notation to the conventional one, $D^{(L)}$ or D_L, introduced by Wigner (*D* for *Darstellung*) for representations of the rotation group. Using Eq. (4-6), we can compute the characters of all the classes of group elements. The results are simply

$$\chi(C_2) = \chi(\pi) = (-1)^L$$

$$\chi(C_3) = \chi\left(\frac{2\pi}{3}\right) = \begin{cases} 1 & L = 0, 3, \ldots \\ 0 & L = 1, 4, \ldots \\ -1 & L = 2, 5, \ldots \end{cases} \tag{4-10}$$

$$\chi(C_4) = \chi\left(\frac{\pi}{2}\right) = \begin{cases} 1 & L = 0, 1, 4, 5, \ldots \\ -1 & L = 2, 3, 6, 7, \ldots \end{cases}$$

Since the spherical harmonics of order L form a basis for representing the group of *all* rotations, they certainly do so for the finite group of rotations O. In fact, we expect that we may be able to reduce the representation into smaller irreducible ones for this smaller group. To do this formally, we merely need the character of D_L together with the decomposition formula (3-20). For convenience, we tabulate the characters of the first few of these (perhaps) reducible representations of O. Then, using (3-20),

$$D_L = \sum_i a_i \Gamma_i \qquad \text{where} \qquad a_i = (24)^{-1} \sum_k N_k \chi_i(\mathscr{C}_k) \chi_L(\mathscr{C}_k)$$

For the simpler cases, we can decompose the representation by inspection by noting what rows from the irreducible representation table need to be added together to produce the desired row in the D_L table. Let us list the first few cases:

O	E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
D_0	1	1	1	1	1
D_1	3	0	−1	−1	1
D_2	5	−1	1	1	−1
D_3	7	1	−1	−1	−1
D_4	9	0	1	1	1

$D_0 = A_1$ cannot split since it is only one-dimensional.

$D_1 = T_1$, by comparison of the characters. Since D_1 remains a single irreducible representation, a P state ($L = 1$) is not split by a cubic field.

$D_2 = E + T_2$. D_2 *must* split, since there are no five-dimensional *irreducible* representations of O. The actual decomposition shows that a D state ($L = 2$) is split into a twofold and a threefold degenerate level in a cubic field.

$D_3 = A_2 + T_1 + T_2$. Thus an F state is split into a nondegenerate and two threefold degenerate states.

$D_4 = A_1 + E + T_1 + T_2$. Thus a G state splits into a nondegenerate state, a doubly degenerate state, and two triply degenerate states.

These examples show that the degrees of residual degeneracy of an atom in a field of given symmetry may be worked out almost trivially by using group theory. Moreover, the various irreducible representations completely determine the symmetry or transformation properties of the various sets of degenerate eigenfunctions.

Additional splitting in field of lower symmetry. In most actual crystals there are at least small departures from cubic symmetry at the lattice site of a magnetic ion. We could handle such cases by a method exactly analogous to that employed above for the group O, but using the appropriate smaller group. However, we get much more insight into the final level structure by considering the problem in steps, first working out the splitting of the free-ion terms into the irreducible representations of the cubic (octahedral) group, then working out the additional smaller splitting of these representations under the field of lower symmetry.

As an example, we have shown that an $L = 2$ state splits into $E + T_2$ under the group O. Now let us assume that the octahedron of ions producing the crystal field is distorted by an elongation along one of the threefold axes. This reduces the rotational symmetry to simply the group D_3, which is a subgroup of O. To find the additional splitting of the E and T_2 levels, we need only decompose these representations, which may be reducible with respect to the subgroup D_3, though irreducible under O. To facilitate this reduction, we write down the character table of D_3 and add to it the characters of the various irreducible representations of O, treated as representations of D_3. This can be done if we note by geometrical inspection that the C_2's of D_3 in this case are the same as the $6C_2$ type of twofold rotations of O. In this way we obtain the following table:

D_3		E	$2C_3$	$3C_2$
Irreducible representations of D_3	A_1	1	1	1
	A_2	1	1	-1
	E	2	-1	0
Irreducible representations of O	A_1	1	1	1
	A_2	1	1	-1
	E	2	-1	0
	T_1	3	0	-1
	T_2	3	0	1

Comparing the two halves of the table, we see that the one- and two-dimensional representations A_1, A_2, and E are also irreducible under D_3 (even retaining the same labels); so the corresponding energy levels do not split any further under the deviation from cubic symmetry. Of course, the one-dimensional representations could not split in any case, but the result for E is less trivial. Next we note that T_1 and T_2 must split, because there are no three-dimensional representations of D_3. Inspection of the tables or use of the decomposition formula (3-20) shows that

$$T_1 \rightarrow E + A_2$$

$$T_2 \rightarrow E + A_1$$

Thus each triply degenerate level in a cubic field splits into a doubly degenerate and a nondegenerate level under a trigonal distortion along one of the threefold axes of O. (If the trigonal axis were *not* one of these axes, then the residual symmetry in the presence of both fields would be smaller than either group and might contain only the identity. In this case, all the orbital degeneracy would be lifted.)

The results which we have obtained are shown schematically in Fig. 4-7. Naturally it is impossible to know the order of the levels without knowledge of at least the sign of the perturbing fields. Such information can be obtained, as noted above, from a rough estimate of the crystalline potential. By perturbation methods, one can find the *ratios* of splittings produced by a given potential (such as the ratio $[E(T_2) - E(T_1)]/[E(T_1) - E(A_2)]$ for the $L = 3$ case) even if the magnitude of the crystal field is known only roughly. We shall not go into this here, but it has been treated by Bethe and by more recent authors such as Bleaney and Stevens.

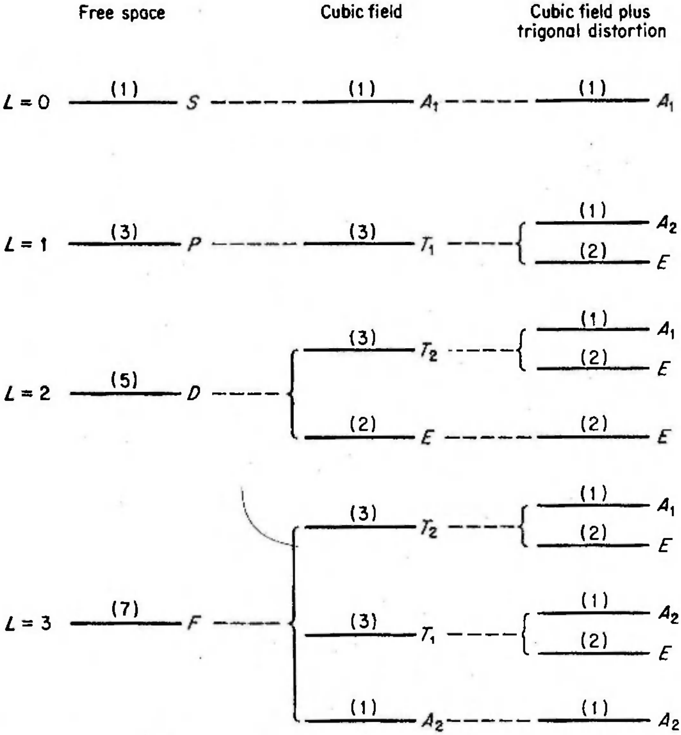
Free space
Cubic field
Cubic field plus trigonal distortion
L = 0
(1)
S
(1)
A1
(1)
A1
L = 1
(3)
P
(3)
T1
(1)
A2
(2)
E
L = 2
(5)
D
(3)
T2
(1)
A1
(2)
E
(2)
E
(2)
E
L = 3
(7)
F
(3)
T2
(1)
A1
(2)
E
(3)
T1
(1)
A2
(2)
E
(1)
A2
(1)
A2

Fig. 4-7. *Scheme of crystal-field splittings for various orbital angular-momentum states. The parenthetical numbers give the degeneracies of the various levels.*

Case of two inequivalent electrons. If we are considering an atom with two electrons outside filled shells, we can form a direct product representation of the symmetry group with basis functions $\psi(1)\varphi(2)$. If the electrons are "inequivalent," i.e., if they belong to different nl subshells, the exclusion principle is satisfied for all possible product functions and no complications arise. (More precisely, a nonvanishing antisymmetrized product can be formed from any such pair. See below.)

Consider the example of a $2p3p$ configuration, in which we have two inequivalent p electrons, situated in a cubic field. The character of the nine-dimensional representation $\mathscr{D} = D_1 \times D_1$ is simply found by taking the product of the character of D_1 with itself. The result is:

O	E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
$D_1 \times D_1$	9	0	1	1	1

Decomposing this by our formula, we find that

$$D_1 \times D_1 = A_1 + E + T_1 + T_2$$

Thus our example state is split into one onefold, one twofold, and two threefold levels under a cubic field. This behavior should be contrasted with the fact that a single p-electron state is unsplit by a cubic field.

It is worthwhile to anticipate the results of the next chapter, in which we put the elementary vector model on a rigorous group-theoretical foundation. Then we shall see that $D_1 \times D_1 = D_0 + D_1 + D_2$. This is the familiar result that two inequivalent p electrons can couple vectorially to produce either an S, a P, or a D state. If we then subject these coupled, two-electron states to the cubic field and use the results of the previous sections, we reach the same final result: $A_1 + E + T_1 + T_2$.

Case of equivalent electrons. In a complete group-theoretical approach, we need to include *all* the symmetries of the system. We are still neglecting the permutation symmetry of the electrons, essentially treating them as if they were distinguishable. In fact the identity of the electrons requires that the state function Ψ be totally antisymmetric under interchange of two electrons (Pauli principle). This symmetry could be handled by recourse to the permutation group, as is done in Wigner's book. However, when we really cope with this problem, we shall follow the usual current practice of writing all wavefunctions (including spin explicitly) in an antisymmetrized form. This automatically eliminates states which are inconsistent with the Pauli principle. For the time being we shall simply rely on the usual elementary arguments for determining which states allowed by the vector model are also consistent with the Pauli principle. For example, with two equivalent p electrons (an np^2 configuration), the only allowed triplet state is a ${}^3P$ state. Since the definition of a P state is basically that its three degenerate substates transform under rotations like a single p electron, we can simply apply all the results of our previous sections. Thus ${}^3P \to {}^3T_1$, and the triplet state is not split in a cubic field. ${}^1S$ and ${}^1D$ states can also be formed from an np^2 configuration, but according to Hund's rules, they will have higher energies than the triplet state. In the presence of a cubic field, the ${}^1S$ is unsplit, but the ${}^1D$ splits into ${}^1E + {}^1T_2$, as noted above.

Physical picture for splittings. Consider a cubic field produced by six ions located at the vertices of a regular octahedron surrounding the ion under consideration. The coordinate axes are chosen to pass through these ions. Under these circumstances it is obvious that the three p functions (p_x, p_y, p_z) are subjected to completely equivalent fields, and no splitting can occur. Now, if we lower the symmetry by pulling the ions on the z axis further out, we introduce a term of the type $(3z^2 - r^2)$ in the potential and make the p_z orbital inequivalent to the p_x, p_y pair. This leaves us with two separate representations: a one-dimensional one based on p_z and a two-dimensional one based on (p_x, p_y). These smaller sets of functions now form bases for representations because we have reduced the size of the symmetry group by removing all symmetry operators which interchanged the z direction with x or y.

If we consider d functions, there *is* a splitting by a cubic field. A suitable choice of d functions for cubic symmetry is the set of three which transform like (xy, yz, zx) and form a basis for T_2, together with the set of two transforming like $(x^2 - y^2)$, $(3z^2 - r^2)$ which form a basis for E. (This set of five functions differs from the set of Y_2^m's only by a unitary transformation.) Considering contours of these functions, we see that the T_2 functions have lobes which avoid the surrounding octahedron of ions, whereas the E functions point straight at them. Therefore, if the ions are repulsive centers, the T_2 functions lie lower in energy than those of E. If one considers the various operations of the cubic group O, one finds that they merely scramble the T_2 and E functions (separately) among themselves. No mixing occurs between T_2 and E functions, as it would under an *arbitrary* three-dimensional rotation. This is the group-theoretical basis for the possibility of decomposing D_2 into $E + T_2$ under the subgroup O of the full rotation group. A pictorial representation of these functions is given in Fig. 8-7.

4-7 Weak-crystal-field Case and Crystal Double Groups

In this case the crystal field is weak compared with the spin-orbit coupling. Hence the *total* angular momentum (including spin) J stays nearly a good quantum number. This allows us to restrict our consideration to a single level of a multiplet, such as $^4F_{\frac{3}{2}}$. If there is an even number of electrons, $J = |\mathbf{L} + \mathbf{S}|$ must be integral, $(2J + 1)$ is odd, and we may handle the splittings by exactly the same procedure as used when we considered only the orbital angular momentum L. If there is an odd number of electrons, however, J is half integral, $(2J + 1)$ is even, and we have to deal with representations of the full rotation group which are not offered by the spherical harmonics. In fact we must introduce the concept of *spinors* to handle these cases. These introduce the two-valued representations mentioned at the end of Sec. 4-4. These will be dealt with in detail in the next chapter. For the time being we shall follow a procedure introduced by Bethe which allows us to obtain all our results by a simple extension of our standard analysis by introducing the concept of *crystal double groups*.

Crystal double groups. In this approach we anticipate the fact (which we prove in the next chapter) that our formula (4-6) for the character of a rotation is valid whether the angular momentum J is integral or half integral. Thus, for a rotation through an angle α, we have

$$\chi_J(\alpha) = \frac{\sin (J + \frac{1}{2})\alpha}{\sin (\alpha/2)} \tag{4-11}$$

If we now consider a rotation by $(\alpha + 2\pi)$, we find

$$\chi_J(\alpha + 2\pi) = \frac{\sin (J + \frac{1}{2})(\alpha + 2\pi)}{\sin (\alpha/2 + \pi)} = (-1)^{2J}\chi_J(\alpha)$$

Therefore, for half integral J we have a *double-valued* character, since a rotation by 2π should leave everything unchanged, whereas for these cases $\chi_J(\alpha + 2\pi) = -\chi_J(\alpha)$. Note, however, that even for half integral J

$$\chi_J(\alpha \pm 4\pi) = \chi_J(\alpha)$$

so that the representations act as if a rotation through 4π should be considered the identity. Also note that

$$\chi_J(\pi + 2\pi) = \chi_J(\pi) = 0$$

showing that the character for a twofold rotation is *single*-valued.

We cope with this strange situation by introducing the fiction that the crystal is taken into itself, not under a rotation by 2π, but only after a rotation of 4π. We introduce a new group element R which represents a rotation by 2π and has the property $R \neq E$ but $R^2 = E$. The augmented group contains twice as many elements as the original one and is called the crystal double group. The double group has more classes than the original, but not necessarily twice as many, since $\chi_J(RC_2) = \chi_J(C_2) = 0$, making it possible that RC_2 is in the same class as C_2. Opechowski[1] has shown by a more thorough investigation that RC_2 is in the same class as C_2 if, and only if, there is another twofold axis perpendicular to the one in question. This method of reducing the double-valued representations (i.e., two distinct matrix representations of each symmetry operator, differing in sign) to an apparently single-valued situation bears some analogy to the construction of several-sheeted Riemann surfaces in the discussion of multiple-valued functions. Actually, by using the homomorphism of the three-dimensional rotation group to the unitary group discussed in the next chapter, one can provide quite a straightforward interpretation of the double group. But we shall not go into this here.

Within the framework of the double-group method, we can handle the half integral J's by the same procedure as we developed for the ordinary case. As an example, we treat the octahedral double group O'. This consists of 48 elements: each of the 24 in O together with the 24 new elements obtained by combining each of them with R. In addition to the five classes of O, we have the classes R, $R \cdot C_3$, $R \cdot C_4$. (The RC_2's remain in the same class with the C_2's because there are perpendicular C_2 axes.) Thus we need to add three irreducible representations and 24 elements. This can be done consistently with the dimensionality theorem (3-12) if we keep the five ordinary representations of O ($\Gamma_1 \cdots \Gamma_5$ in Bethe's notation) and add three new ones Γ_6, Γ_7, Γ_8 of dimensionality 2, 2, and 4.

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[1] W. Opechowski, *Physica*, 7, 552 (1940). See also V. Heine, "Group Theory in Quantum Mechanics," p. 137, Pergamon Press, New York, 1960.

In setting up the character table of O' we take advantage of the close relation between O' and O. First of all, we see that we can get the characters of all the "normal" single-valued representations $\Gamma_1 \cdots \Gamma_5$ by simply taking $\chi(RA) = \chi(A)$, where A is any group element. This procedure assures satisfaction of the requirements on orthonormality between rows. In the double-valued representations, we take $\chi(RA) = -\chi(A)$. This assures that the R column is normalized properly and orthogonal to the E column. We also take $\chi(RC_2) = \chi(C_2) = 0$ since $\chi(RC_2) = \chi(C_2)$, because they are in the same class, while $\chi(RA) = -\chi(A)$ for all A in the double-valued representations. The value zero is also required in order to give the correct column normalization. In the exceptional case when there is no perpendicular C_2 axis, leaving RC_2 and C_2 in different classes, both these arguments fail, and $\chi(RC_2) = -\chi(C_2) \neq 0$, in general. With these various aids and rules, one quite readily can work out the character tables, such as that of O' given below.

O'	E	R	$8C_3$	$8RC_3$	$3C_2 + 3RC_2$	$6C_2 + 6RC_2$	$6C_4$	$6RC_4$
Γ_1	1	1	1	1	1	1	1	1
Γ_2	1	1	1	1	1	−1	−1	−1
Γ_3	2	2	−1	−1	2	0	0	0
Γ_4	3	3	0	0	−1	−1	1	1
Γ_5	3	3	0	0	−1	1	−1	−1
Γ_6	2	−2	1	−1	0	0	$\sqrt{2}$	$-\sqrt{2}$
Γ_7	2	−2	1	−1	0	0	$-\sqrt{2}$	$\sqrt{2}$
Γ_8	4	−4	−1	1	0	0	0	0

Application of double groups to term splittings. For integral J, $\chi_J(RC) = \chi_J(C)$, and the character is orthogonal to the characters of all the new double-valued irreducible representations. Accordingly, the decomposition is entirely into the normal single-valued representations, and it works out exactly as it would if the group had not been "doubled."

For half integral J we have seen that $\chi_J(RC) = -\chi_J(C)$ for arbitrary rotations. Thus the character will be orthogonal to those of the single-valued representations, and the decomposition is wholly into the new double-valued representations (Γ_6, Γ_7, and Γ_8 for O').

Evaluating characters for half integral J with Eq. (4-11), we find:

O'	E	R	$8C_3$	$8RC_3$		$3C_2 + 3RC_2$	$6C_2 + 6RC_2$	$6C_4$	$6RC_4$	
D_J	$(2J+1)$	$-(2J+1)$	1	-1	$(J = \frac{1}{2}, \frac{7}{2}, \cdots)$	0	0	$\sqrt{2}$	$-\sqrt{2}$	$(J = \frac{1}{2}, \frac{9}{2}, \cdots$
			-1	1	$(J = \frac{3}{2}, \frac{9}{2}, \cdots)$			0	0	$(J = \frac{3}{2}, \frac{7}{2}, \frac{11}{2},$
			0	0	$(J = \frac{5}{2}, \frac{11}{2} \cdots)$			$-\sqrt{2}$	$\sqrt{2}$	$(J = \frac{5}{2}, \frac{13}{2}, \cdots$

If we use these results in the standard decomposition formula, we find the results tabulated below:

$$D_{\frac{1}{2}} \rightarrow \Gamma_6$$

$$D_{\frac{3}{2}} \rightarrow \Gamma_8$$

$$D_{\frac{5}{2}} \rightarrow \Gamma_7 + \Gamma_8$$

$$D_{\frac{7}{2}} \rightarrow \Gamma_6 + \Gamma_7 + \Gamma_8$$

$$D_{\frac{9}{2}} \rightarrow \Gamma_6 + 2\Gamma_8$$

. . . .

Thus levels with $J = \frac{1}{2}$ or $\frac{3}{2}$ are unsplit in a cubic field; a $J = \frac{5}{2}$ level splits into a doublet and a quartet, and so on. We note that all the extra double-valued representations are of even dimension, and hence of dimension greater than 1. Therefore all levels are at least twofold degenerate. This result can be proved (see Sec. 5-16) in general for half-integral angular momenta (odd number of electrons) for an electric field of any symmetry since it is a consequence of time reversal symmetry. This is known as *Kramers' theorem.*[1] It plays an important role in the theoretical interpretation of paramagnetic-resonance experiments.

4-8 Introduction of Spin Effects in the Medium-field Case

In our previous treatment of this case (Sec. 4-6), we neglected spin effects completely and merely found the orbital-level structure. In addition to the residual degeneracies found there, we still had the $(2S + 1)$-fold spin degeneracy. If the spin-orbit and spin-spin couplings are now introduced so that the spins can "feel" the symmetry of the lattice through the orbital motion, second-order effects arise which may split the spin degeneracy. We can find out about this by introducing direct-product representations based on products of orbital and spin functions.

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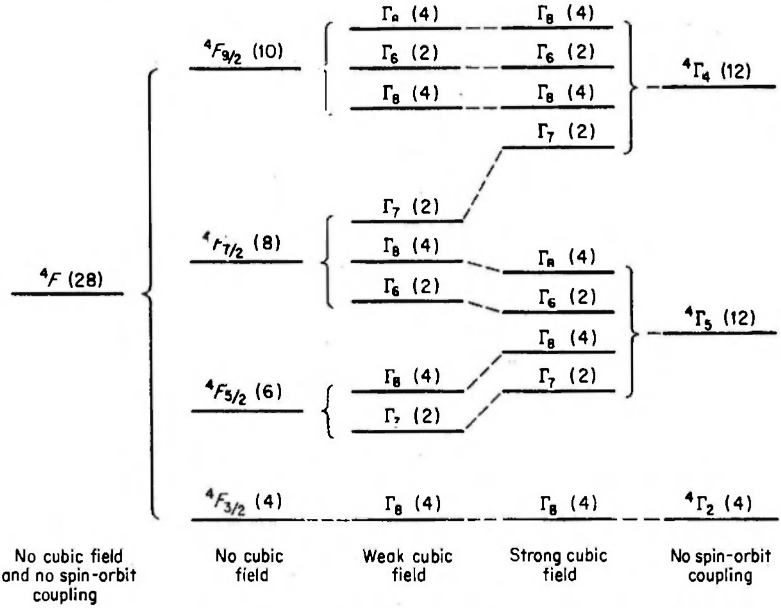
[1] H. Kramers, *Proc. Acad. Sci. Amsterdam*, **33**, 959 (1936).

For example, consider the splitting of a ^4F term in a cubic crystal field. As noted earlier, the orbital F state splits according to $D_3 = A_2 + T_1 + T_2 = \Gamma_2 + \Gamma_4 + \Gamma_5$. Each of these representations is now to be combined with the representation $D_{\frac{3}{2}} = \Gamma_8$ of the spin. Using the decomposition formula to decompose the direct-product representations, we find



$^4F_{9/2}$ (10)
$^4F_{7/2}$ (8)
^4F (28)
$^4F_{5/2}$ (6)
$^4F_{3/2}$ (4)
Γ_8 (4)
Γ_6 (2)
Γ_8 (4)
Γ_7 (2)
Γ_8 (4)
Γ_6 (2)
Γ_8 (4)
Γ_7 (2)
Γ_8 (4)
Γ_8 (4)
Γ_6 (2)
Γ_8 (4)
Γ_7 (2)
Γ_8 (4)
Γ_6 (2)
Γ_8 (4)
Γ_7 (2)
Γ_8 (4)
$^4\Gamma_4$ (12)
$^4\Gamma_5$ (12)
$^4\Gamma_2$ (4)
No cubic field and no spin-orbit coupling
No cubic field
Weak cubic field
Strong cubic field
No spin-orbit coupling

Fig. 4-8. *Variation of level structure of ^4F term with increasing cubic-field strength compared with spin-orbit coupling strength. The parenthetical numbers give the degeneracies of the various levels.*

$$
\begin{aligned}
\Gamma_2 \times \Gamma_8 &= \Gamma_8 \\
\Gamma_4 \times \Gamma_8 &= \Gamma_6 + \Gamma_7 + 2\Gamma_8 \\
\Gamma_5 \times \Gamma_8 &= \Gamma_6 + \Gamma_7 + 2\Gamma_8
\end{aligned}
$$

This shows that the Γ_2 level keeps its fourfold spin degeneracy, whereas the Γ_4 level, for example, splits into four distinct levels of degeneracy 2, 2, 4, and 4.

It is instructive to combine these results with the results of the previous two sections in a schematic diagram (Fig. 4-8) showing the level structure of a ^4F term under a cubic field of various strengths compared with the spin-orbit coupling. Note that the irreducible representations of the double group serve as rigorous good quantum numbers under all conditions shown. However, if either the crystal field or the spin-orbit coupling is set to zero, a number of these representations coalesce into larger representations, as shown. In any case, of course, the total number of states remains invariant under all types of splitting. We note that a remarkable amount of information about the level structure has been obtained by group-theoretical considerations of symmetry alone.

4-9 Group-theoretical Matrix-element Theorems

In Sec. 3-8 we proved that two functions $\varphi_\kappa^{(j)}$ and $\psi_{\kappa'}^{(j')}$ which belong to different irreducible representations or to different rows of the same unitary representation are orthogonal. Moreover, we showed that the scalar product $(\varphi_\kappa^{(j)}, \psi_\kappa^{(j)})$ was independent of κ. This result is easily generalized to the following theorem:

Matrix elements of an operator H which is invariant under all operations of a group vanish between functions belonging to different irreducible representations or to different rows of the same unitary representation.

This theorem follows from the simple orthogonality result quoted first, by simply noting that the invariance of H means that H belongs to Γ_1, the identical representation. In this case, $H\varphi_\kappa^{(j)}$ belongs to the direct-product representation, $\Gamma_1 \times \Gamma^{(j)} = \Gamma^{(j)}$, as can be shown formally by noting that $\chi_1(R) = 1$ for all operators R. Physically speaking, it is apparent that application of an operator which is so symmetrical as to be invariant under all group operations will leave the symmetry of $\varphi_\kappa^{(j)}$ completely unchanged with respect to all group operations. Hence $H\varphi_\kappa^{(j)}$ also belongs to the κth row of the jth irreducible representation, and the matrix-element theorem for invariant operators follows from the orthogonality proof. Moreover, the equality for all κ of the scalar products $(\varphi_\kappa^{(j)}, \psi_\kappa^{(j)})$ carries over to the equality of the diagonal-type matrix elements $(\varphi_\kappa^{(j)}, H\psi_\kappa^{(j)})$. Hence, if we choose the set $\psi_\kappa^{(j)}$ to be actually identical with the $\varphi_\kappa^{(j)}$ and take H to be the Hamiltonian operator, we have the result that all basis-function partners within a given irreducible representation have the same energy. This is consistent with the way we originally connected the representation theory with quantum mechanics. Of equal importance is the fact that the absence of *any* matrix elements of H connecting states of different symmetry (representation indices) guarantees the rigor of these group-theoretical quantum numbers, regardless of the order to which one might carry perturbation theory. Accordingly, our symmetry-based results on splittings and selection rules will retain their ultimate accuracy.

Generalized Unsöld theorem. In connection with the preceding theorem about invariant operators, it is of some interest to consider the following theorem, which prescribes a method of generating invariant functions. The theorem states that the sum $\sum_{\kappa=1}^{l_j} |\varphi_\kappa^{(j)}|^2$ is invariant under all operations of the group for which the $\varphi_\kappa^{(j)}$ form the basis of an irreducible representation. This is a generalization of the theorem originally given by Unsöld, which states that $\sum_{m=-l}^{l} |Y_l^m(\theta, \varphi)|^2$ is invariant under all rotations; i.e., closed shells of atoms have spherical symmetry.

We prove the theorem by evaluating the effect on the sum of applying an arbitrary transformation operator from the group. Thus, we consider

$$\begin{aligned} P_R \sum_\kappa |\varphi_\kappa^{(j)}|^2 &= P_R \sum_\kappa \varphi_\kappa^{(j)*}\varphi_\kappa^{(j)} \\ &= \sum_{\mu\lambda\kappa} \varphi_\mu^{(j)*}\Gamma^{(j)}(R)^*_{\mu\kappa}\varphi_\lambda^{(j)}\Gamma^{(j)}(R)_{\lambda\kappa} \\ &= \sum_{\mu\lambda} \varphi_\mu^{(j)*}\varphi_\lambda^{(j)} \sum_\kappa \Gamma^{(j)}(R)_{\lambda\kappa}\Gamma^{(j)}(R^{-1})_{\kappa\mu} \end{aligned}$$

since the representation is unitary. Noting that the sum on κ is just $\Gamma^{(j)}(E)_{\lambda\mu} = \delta_{\lambda\mu}$, we find that

$$P_R \sum_\kappa |\varphi_\kappa^{(j)}|^2 = \sum_\mu |\varphi_\mu^{(j)}|^2 = \sum_\kappa |\varphi_\kappa^{(j)}|^2$$

and the theorem is proved.

As a simple example of the theorem, recall that the three functions x, y, and z form a basis for the representation T_1 of the group O. The sum of the squares of these is $x^2 + y^2 + z^2 = r^2$, which is invariant under *all* rotations and therefore certainly under all the rotations comprising O.

A less trivial example is provided by the functions xy, yz, and zx which form a basis for T_2 of O. In this case, the sum of squares is $x^2y^2 + y^2z^2 + z^2x^2$. This function is invariant under all operations of O and hence belongs to $A_1(\equiv \Gamma_1)$. Note that

$$\tfrac{2}{5}(x^2 + y^2 + z^2)^2 - 2(x^2y^2 + y^2z^2 + z^2x^2) = (x^4 + y^4 + z^4 - \tfrac{3}{5}r^4)$$

Thus, apart from an additive term of spherical symmetry, the invariant function generated here is equivalent to the form of the cubic field potential V_0 given in Eq. (4-7).

Matrix-element selection rules. In the first part of this section, we proved an important theorem on matrix elements of invariant operators. In many problems one is also interested in matrix elements of perturbations which are not invariant under all group operations. These may be static perturbations which lower the symmetry below that of the unperturbed problem, or they may be time-dependent perturbations by radiation which induce transitions. The symmetry considerations are the same in either case.

What we seek is a selection rule which restricts the variety of matrix elements between different irreducible representations according to the symmetry of the perturbing operator H'. To obtain this selection rule, we first determine the irreducible representation $\Gamma_{H'}$ according to which H' transforms. [In a general case, H' may contain parts of different symmetries. We may always decompose it, however, according to an analog of Eq. (3-33).] Having found $\Gamma_{H'}$, we note that $H'\varphi_\kappa^{(j)}$ will belong to representations included in $\Gamma_{H'} \times \Gamma^{(j)}$. Then, by the basis-function orthogonality theorem, *the matrix element* $(\psi_{\kappa'}^{(j')}, H'\varphi_\kappa^{(j)})$ *must be zero unless* $\Gamma^{(j')}$ *is found in* $\Gamma_{H'} \times \Gamma^{(j)}$. An equivalent statement is that the matrix element must vanish unless $\Gamma^{(j')*} \times \Gamma_{H'} \times \Gamma^{(j)}$ includes Γ_1, the identical representation. The latter form follows from the observation that a matrix element is invariant under any unitary transformation P_R of the integrand $\psi_{\kappa'}^{(j')*}H'\varphi_\kappa^{(j)}$. If we sum over all P_R and use the orthogonality of all other $\Gamma^{(j)}(R)_{\kappa\lambda}$ to $\Gamma_1(R) = 1$, we have the result.

Note that the theorem proved earlier in the section is a special case of the general matrix-element theorem just proved. We should also emphasize that this theorem does *not* guarantee the *existence* of any matrix elements. Rather, it *excludes* the possibility of some kinds. To make a more complete prediction based on symmetry alone, one would need to take advantage of the row index κ as well as the representation label j. For example, if $H' \sim x$ and $\varphi_\kappa^{(j)} \sim y$, we have $\Gamma_{H'} = \Gamma^{(j)} = T_1$ of the group O. Taking $T_1 \times T_1$, we obtain $T_1 + T_2 + E + A_1$. Yet $H'\varphi_\kappa^{(j)} \sim xy$ belongs to T_2 alone. Thus, only if $\Gamma^{(j')} = T_2$ can the matrix element $(\psi_{\kappa'}^{(j')}, H'\varphi_\kappa^{(j)})$ differ from zero, and then only if κ' is the xy row index of T_2. In the absence of such a detailed examination, one can say only that, if one considered functions with all the possible symmetries allowed by the representation labels alone, then matrix elements of all the types allowed by the theorem would occur (barring any fortuitous cancellations for specially chosen values of parameters).

4-10 Selection Rules and Parity

The transition probability per unit time in the presence of a perturbation is given by the famous "Golden Rule formula"[1]

$$w = \frac{2\pi}{\hbar}\,\rho(k)\,|H'_{km}|^2 \tag{4-12}$$

where $\rho(k)$ is the density of final states in energy and H'_{km} is the matrix element of the perturbative Hamiltonian H' which connects the initial state

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[1] L. I. Schiff, "Quantum Mechanics," 2d ed., p. 199, McGraw-Hill Book Company, Inc., New York, 1955. Note that in using this formula a consistent normalization volume must be used for $\rho(k)$ and H'_{km}.

m with the final state k. For electric-dipole transitions, $H' = e\mathbf{r} \cdot \mathbf{E} \sim e\mathbf{p} \cdot \mathbf{A}/c$. Since the field $\mathbf{E}$ is determined externally by the radiation inducing the transition, the transition probability under given conditions is proportional to $|\mathbf{r}_{km}|^2$ or $|\mathbf{p}_{km}|^2$. Similarly, for magnetic-dipole transitions, $w \sim |\boldsymbol{\mu}_{km}|^2 = \beta^2 \, |(2\mathbf{S} + \mathbf{L})_{km}|^2$, where $\boldsymbol{\mu}$ is the magnetic-moment operator and β is the Bohr magneton. For electric-quadrupole transitions, we have to find matrix elements of quadratic forms of coordinates which couple to gradients in the exciting field. For most purposes, however, we may confine our attention to the dipole coupling terms. We now consider how our matrix-element selection rule governs the allowed dipole transitions.

Electric-dipole transitions. The electric-dipole-moment operator $e\mathbf{r}$ is a *polar vector* (V). This means that its components transform like the coordinates. For example, in a rotation through φ about the z axis

$$\mathbf{\Gamma}^V(\varphi) = \begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{4-13a}$$

gives the transformation properties of the x, y, z components. From this we see that the character is

$$\chi^V(\varphi) = 1 + 2\cos\varphi \tag{4-14a}$$

This result is true for rotations by φ about any axis, since they are all in the same class.

If we now combine an inversion with the rotation by φ, then the matrix changes sign to

$$\mathbf{\Gamma}^V(\varphi, i) = \begin{pmatrix} -\cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & -\cos\varphi & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{4-13b}$$

so that

$$\chi^V(\varphi, i) = -(1 + 2\cos\varphi) \tag{4-14b}$$

Knowing the character under an arbitrary proper or improper rotation, we can find what representation a polar vector belongs to for any given group. Of course, the three-dimensional representation Γ^V may decompose into more than one irreducible representation. In fact it *must* decompose if the group under consideration has no three-dimensional irreducible representations.

Magnetic-dipole transitions. The magnetic-dipole-moment operator $\boldsymbol{\mu}$ is an *axial vector* (A), or *pseudovector*. This means that it transforms like a (polar) vector under rotations but is *invariant under inversion*. This is true because, for example, $\boldsymbol{\mu} \sim \mathbf{L} \sim \mathbf{r} \times \mathbf{p} \sim m\mathbf{r} \times d\mathbf{r}/dt$. The two sign changes as $\mathbf{r} \rightarrow -\mathbf{r}$ cancel, leaving the product invariant. An axial vector is really a skew-symmetric tensor of rank 2. From these properties,

$$\mathbf{\Gamma}^A(\varphi, i) = \mathbf{\Gamma}^A(\varphi) = \begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{4-15}$$

and

$$\chi^A(\varphi, i) = \chi^A(\varphi) = 1 + 2\cos\varphi \tag{4-16}$$

Examples. In the group $O_h = O \times i$, we know that (x, y, z) and hence any polar vector V transforms as T_{1u}. Similarly, an axial vector A transforms as T_{1g} since it has the same rotational properties as V but is even under inversion. These results can be checked by using the characters above together with the character table of O_h.

In our example group D_3, we do not have inversion symmetry, and parity is not a good quantum number. V and A act the same under all operations of the group. Using (4-16), $\chi(E) = 3$, $\chi(C_2) = 1 + 2\cos\pi = -1$, $\chi(C_3) = 1 + 2\cos(2\pi/3) = 0$. Decomposing this character, we find

$$\Gamma^V = \Gamma^A = A_2 + E$$

Actually, we have noted earlier that z belongs to A_2 and (x, y) belongs to E. Thus we can say that A_2 determines the selection rules for radiation polarized along z, while E determines selection rules for radiation polarized in the xy plane.

Inversion and parity. Until now, we have skirted the question of the inversion operator i. We have concentrated our attention on the point groups composed only of proper rotations. In many groups which actually interest us, we do in fact have inversion symmetry. In handling these, we take advantage of the fact that i commutes with all other operators in our group. This allows us to consider the full group as a direct product and to write the character table directly. This point was illustrated rather fully in the example of Sec. 3-9, except that in that example we considered the group (σ_h, E) rather than (i, E). Thus, in the present instance, we combine the two tables

$\mathcal{G}$	$\mathcal{C}_1 \cdots \mathcal{C}_r$
Γ_1	
$\cdots$	χ
Γ_r	

and

i	E	i
g	1	1
u	1	-1

to obtain the table

$\mathcal{G} \times i$	$\mathscr{C}_1 \cdots \mathscr{C}_r$	$i\mathscr{C}_1 \cdots i\mathscr{C}_r$
Γ_{1g} $\cdots$ Γ_{rg}	χ	χ
Γ_{1u} $\cdots$ Γ_{ru}	χ	$-\chi$

In the free atom we certainly have inversion symmetry in the Hamiltonian (for all the terms concerning the electrons at least!). Therefore parity is a good quantum number, and all atomic states will be either pure *g* or pure *u*. Actually the conventional notation for parity in atoms is + and — rather than *g* and *u*. The parity of a one-electron wavefunction is $(-)^l$, where l is the orbital angular-momentum quantum number. In a many-electron atom, therefore, it is $\prod_k (-)^{l_k}$, where k runs over all the electrons. In other words, $\chi(i) = \prod_k (-1)^{l_k}$.

Now, if we place such an atomic state in a crystal field, we may calculate the character of its representation with respect to the operators of the full symmetry group, including the inversion (if present). When this character is decomposed into those of the irreducible representations of the crystal group, it is obvious that only *g* representations will be found if the atomic state was *g* (or +) and similarly for *u* (or —). This follows from the "evenness" and "oddness" of the upper and lower halves of the character table, respectively. *Thus we conclude that g terms split only into g terms and u terms split only into u terms.* Moreover, since the left and right halves of the character table are identical, except for a possible uniform sign change, by using both halves we merely repeat each term in the sum which occurs in the orthonormality relations and the decomposition formulas. *Thus we can work out all splittings successfully by simply considering the group of proper rotations.* This validates our previous work on the cubic group, for example, where we restricted our attention to O, not O_h.

Parity, or inversion symmetry, does play a vital role in the determination of selection rules, however. The electric-dipole operator belongs to a *u* representation. Therefore our selection-rule theorem tells us that transitions are forbidden between states of the same parity (since $\Gamma_u \times \Gamma$ has the opposite parity to Γ and therefore cannot contain any representations of the same parity as Γ). But the argument of the preceding paragraph shows that the parity is invariant under crystal field splittings. Therefore, *if the crystal field has inversion symmetry, all electric-dipole transitions within the level structure arising from a single free-atom term are forbidden.*

On the other hand, since the magnetic-moment operator is an *axial* vector, it is a Γ_g. Therefore, *magnetic-dipole transitions within a term are not forbidden by parity.* Many of these transitions will be forbidden by other symmetry properties, however. We can find those which are *not* forbidden by considering direct products, as shown in the previous section.

For example, in D_3 we found that μ_z belonged to A_2, and (μ_x, μ_y) to E. Then it is not forbidden that z-polarized radiation will induce transitions between any Γ_i and $\Gamma_i \times A_2$. Taking all possible products,

$$A_1 \times A_2 = A_2 \qquad A_2 \times A_2 = A_1 \qquad E \times A_2 = E$$

Hence the allowed transitions are

$$A_2 \leftrightarrow A_1 \qquad E \leftrightarrow E$$

For radiation polarized in the xy plane,

$$A_1 \times E = E \qquad A_2 \times E = E \qquad E \times E = A_1 + A_2 + E$$

and transitions are allowed between all states and those belonging to E.

Many of the cases of importance in crystal-field splittings have been treated along these lines by Kittel and Luttinger.[1] Actually more recent theoretical research[2] indicates that the optical transitions between crystal-field split levels which cause crystals of paramagnetic salts to have characteristic colors are not predominantly magnetic-dipole transitions but instead are weak electric-dipole transitions. These are possible because vibrations of the ions in the physical crystal destroy the perfect inversion symmetry of the ideal crystal, leaving parity not quite a good quantum number. Since electric-dipole transitions are normally of order $(1/\alpha)^2 \sim (137)^2$ times as intense as magnetic-dipole transitions, even a small breakdown in the parity selection rule allows the electric-dipole transitions to dominate.

Atomic selection rules. The above argument showing that electric-dipole transitions require a parity change is valid *a fortiori* in atoms where the inversion symmetry is perfect (with interatomic interactions and collisions neglected). In a one-electron atom, where $\chi(i) = (-1)^l$, this requires a change of an odd number of units in l. We shall see in the next chapter that rotational symmetry requires that $|\Delta l| \leqq 1$ for a dipole transition.

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[1] C. Kittel and J. M. Luttinger, *Phys. Rev.*, **73**, 162 (1948).

[2] A. D. Liehr and C. J. Ballhausen, *Phys. Rev.*, **106**, 1161 (1957); R. A. Satten, *J. Chem. Phys.*, **27**, 286 (1957), **29**, 658 (1958); C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Company, Inc., New York, 1962.

Combining these two requirements, we obtain the selection rule $\Delta l = \pm 1$ for one-electron atoms, which is well obeyed in practice.

4-11 Directed Valence

In this section we want to explain the symmetries found in molecular binding in terms of those of the available atomic orbitals. For example, why does carbon like tetrahedral and trigonal bonding? Alternatively, given a set of bond angles determining a configuration, we wish to find out what types of orbitals play a role in the binding. This type of question—that of chemical valence—can be approached from two different approximate methods: *molecular orbitals* (Mulliken, Lennard-Jones, and others), in which one-electron eigenfunctions extending over the entire molecule are taken as basis functions; and the Heitler-London-Pauling method of *valence orbitals*, localized in the region between the cores of the atoms being bonded. When carried to a high enough order of approximation, both lead to the same results. Both have their own strong points. For the present discussion, which is intended primarily as another example of the application of group theory, we shall use the valence orbital method. We shall give a more thorough discussion of molecular binding in Chap. 7.

In this method the binding energy may be viewed as arising from the fact that interference terms in the electronic wavefunction, arising from the exchange equivalence of all electrons, cause charge to pile up in the region of low potential energy between the nuclei. The extent to which this occurs is roughly proportional to the amount of overlap between the functions based on the two centers. This leads to Pauling's *overlap criterion* of bond strength. Thus the problem to which we shall apply our group-theoretical machinery is the working out of all possible sets of atomic orbitals from which a set of these overlapping, directed valence orbitals can be formed.

Tetrahedral carbon. As an elementary example of the things we are looking for, let us look into the familiar tetrahedral bonding of carbon, as found in CH_4, for example. The ground state of atomic C is $1s^2 2s^2 2p^2$. We expect the $1s$ shell to be undisturbed by binding; so we have to deal only with $2s$ and $2p$ functions. Neglecting the different radial dependences, and normalizing to 4π over a sphere, these have the forms

$$\begin{aligned} s = 1 \qquad p_x &= \sqrt{3}\sin\theta\cos\varphi \\ p_y &= \sqrt{3}\sin\theta\sin\varphi \\ p_z &- \sqrt{3}\cos\theta \end{aligned}$$

where θ and φ are the usual polar coordinates. We wish to form four linear combinations of these four functions which are equivalent in all ways except that each is directed along a different one of the four tetrahedral directions. A little consideration of symmetry properties leads to

$$\begin{aligned}
\psi_{111} &= \tfrac{1}{2}(s + p_x + p_y + p_z) \\
\psi_{1,-1,-1} &= \tfrac{1}{2}(s + p_x - p_y - p_z) \\
\psi_{-1,1,-1} &= \tfrac{1}{2}(s - p_x + p_y - p_z) \\
\psi_{-1,-1,1} &= \tfrac{1}{2}(s - p_x - p_y + p_z)
\end{aligned}$$

The indices on ψ indicate the direction numbers of the major lobe of the function with respect to the axes of the cube in which the tetrahedron is inscribed. These four orthogonal functions are called the tetrahedral sp^3 *hybrid orbitals.* Under the operation of the group T_d these functions transform only among themselves. Thus they form a basis for a (reducible) representation of T_d. We shall use this property in our later discussion.

A simple measure of overlap and hence of bond strength is the numerical value of the angular function along the bond axis where it is at a maximum. Along the (111) direction, $\cos\theta = 1/\sqrt{3}$, $\sin\theta = \sqrt{2/3}$, and $\sin\varphi = \cos\varphi = 1/\sqrt{2}$. Therefore $p_x = p_y - p_z = \sqrt{3}/\sqrt{3} = 1$ along the (111) direction. Combining this with $s = 1$, we have $\psi_{111}(111 \text{ axis}) = \tfrac{1}{2}[1 + 1 + 1 + 1] = 2$. It is easily verified that all four of the hybrid orbitals have this value along their own axes. This must be true if they have the required degree of symmetry. Further analysis shows that these orbitals give the highest bond strength of any which can be formed from s and p functions. This explains why the tetrahedral bonds of C are so common in nature despite the fact that it is necessary to promote a $2s$ electron from the $2s^22p^2$ ground configuration to a $2p$ electron in order to form these functions. The extra binding more than compensates the promotion energy.

Trigonal carbon. Another observed bonding scheme for carbon is the trigonal bond. In this we form three equivalent coplanar bonds separated by angles of 120°. These can be formed as sp^2 hybrids from s, p_x, p_y.

$$\psi_1 = \sqrt{\tfrac{1}{3}}s + \sqrt{\tfrac{2}{3}}p_x \qquad \psi_{2,3} = \sqrt{\tfrac{1}{3}}s - \sqrt{\tfrac{1}{6}}p_x \pm \sqrt{\tfrac{1}{2}}p_y$$

These are orthonormal and transform into each other under the symmetry operations of D_{3h}. The bond strength is $\psi_1(\theta = \pi/2, \varphi - 0) = \sqrt{\tfrac{1}{3}} + \sqrt{2} =$ 1.99. Since this is only slightly below the strength of the tetrahedra bonds, these bonds in the plane are strong. However, perpendicular t the plane we have only p_z, with a bond strength of $\sqrt{3} = 1.73$. This difference accounts qualitatively for the fact that graphite consists of layer with strong internal bonds but weak interlayer bonding.

Another aspect of the bonding problem arises here, namely, the π bond This is contrasted with the σ bonds which we have been considering, i which the charge is axially symmetric about the bond axis. For exampl in ethylene (C_2H_4), we have what chemists call a *double bond* between the two carbons. The first bond is an ordinary σ bond formed by the overlap of two trigonal orbitals, one from each C. The second is a π bond formed by the overlap of the edges of the p_z charge clouds, which are actually pointing normal to the plane of the molecule. These have a relatively weak overlap and so contribute less to the binding energy. [C—C bond energy is ~59 kcal/mole; C═C is ~100 (= 59 + 41) kcal/mole.] The extra bonding is adequate to prevent relative rotation of the two CH_2 groups, which would reduce the overlap of the p_z functions. This ensures that the molecule stays planar.

4-12 Application of Group Theory to Directed Valence

Now that we have built up some feeling for what we are trying to find, let us examine the problem from a group-theoretical viewpoint. The key to the problem of finding suitable directed orbitals is that they must transform into each other under the group operations. Therefore they form a basis for a (generally reducible) representation of the group. By simple geometrical considerations we can work out the character of the bond representation. Knowing the characters of all the irreducible representations based on free-atom functions, we can easily see from which atomic functions suitable hybrids can be formed.

We illustrate with the trigonal-bond case where the full symmetry group is D_{3h}. The character table (from Sec. 3-9, after relabeling and rearranging to the conventional order) is:

	D_{3h}	E	σ_h	$2C_3$	$2S_3$	$3C'_2$	$3\sigma_v$
z^2	A'_1	1	1	1	1	1	1
	A'_2	1	1	1	1	−1	−1
	A''_1	1	−1	1	−1	1	−1
z	A''_2	1	−1	1	−1	−1	1
$(x, y), (xy, x^2 - y^2)$	E'	2	2	−1	−1	0	0
(xz, yz)	E''	2	−2	−1	1	0	0
	σ	3	3	0	0	1	1
	π	6	0	0	0	−2	0

In this we have listed how the p-like functions (x, y, z) and the d-like functions $(z^2, x^2 - y^2, xy, yz, zx)$ transform. Of course s-like functions are invariant under all group operations and so belong to A'_1. We have also included the characters of the σ-bond and π-bond representations. These characters are simply the number of orbitals going into themselves minus the number going into their negatives under a group operation. This fact follows directly from the definition of the representation matrices. We now consider these characters in more detail.

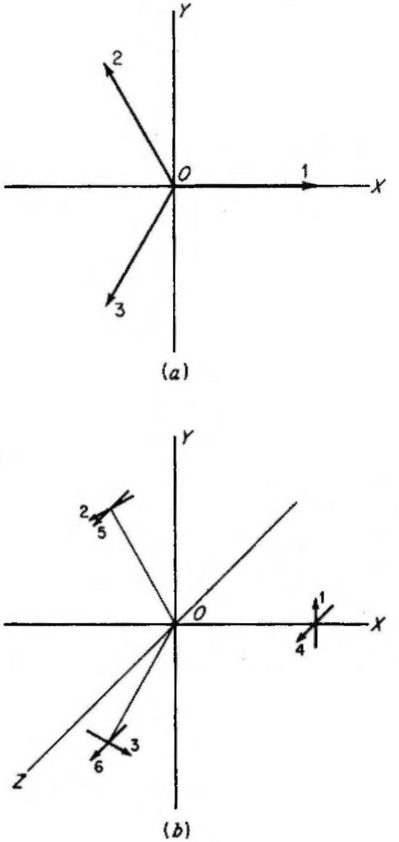

Fig. 4-9. *Schematic representations of (a) the three σ bonds and (b) the six π bonds which arise in a case of trigonal symmetry. In both cases, bonds 1, 2, 3 lie in the xy plane. The arrows representing bonds 4, 5, 6 are perpendicular to the xy plane.*

The three σ bonds can be represented by arrows along the bond axes, as shown in Fig. 4-9*a*. Under E, they all go into themselves, so $\chi^{(\sigma)}(E) = 3$; similarly for σ_h, since the arrows (bonds) are axially symmetric. Unde C_3 and S_3, the threefold rotations change each arrow into another, leavin no diagonal elements in the matrix representation. Thus $\chi^{(\sigma)}(C_3) = \chi^{(\sigma)}(S_3) =$ 0. Under either C_2' or σ_v, two arrows are interchanged, while the thir goes into itself. Therefore $\chi^{(\sigma)}(C_2') = \chi^{(\sigma)}(\sigma_v) = 1$. From this characte system we see that

$$\sigma = A_1' + E'$$

Considering the representations based on the various atomic functions, we see that the set of three σ-bonding orbitals can be made up in four different ways from s, p, and d functions:

sp^2	$s + (p_x, p_y)$
sd^2	$s + (d_{xy}, d_{x^2-y^2})$
dp^2	$d_{z^2} + (p_x, p_y)$
d^3	$d_{z^2} + (d_{xy}, d_{x^2-y^2})$

The group theory assures us that these are the only possible suitable combinations of these functions for the trigonal symmetry.

The π-bonds can be represented (Fig. 4-9*b*) by arrows perpendicular to the bond axis, the arrow indicating the direction of the positive lobe of the transverse function. This scheme suggests the symmetry of functions on the ligand atoms required to overlap with the corresponding central-atom function. In our D_{3h} example, we have six such bonds: 1, 2, 3 are in the xy plane; 4, 5, 6 are parallel to z and point out of the page. By considering the effect of the group operations on these arrows, we work out the character as before. For example, $\chi^{(\pi)}(E) = 6$ because all the arrows go into themselves; $\chi^{(\pi)}(\sigma_h) = 0$ since 1, 2, 3 go into themselves, while 4, 5, 6 go into their negatives. Using the complete character listed as π in the table, we find

$$\pi = A_2' + A_2'' + E' + E''$$

A little inspection shows that the bonds 1, 2, 3 already form a complete basis for $A_2' + E'$, while 4, 5, 6 form a basis for $A_2'' + E''$. This is natural, since 1, 2, 3 are even under σ_h, while 4, 5, 6 are odd, and the representations with single primes are even, while those with a double prime are odd. Since no A_2' functions can be formed from s, p, or d functions, we can properly form only the 4, 5, 6 type of π bond, which is odd on reflection in the xy plane. These require $A_2' + E''$ and hence may be formed only as pd^2 hybrids from the functions p_z, d_{xz}, d_{yz}. The suitable combinations are readily seen to be analogous to those for the trigonal σ bonds, namely,

$$\phi_1 = \sqrt{\tfrac{1}{3}}p_z + \sqrt{\tfrac{2}{3}}d_{xz} \qquad \phi_{2,3} = \sqrt{\tfrac{1}{3}}p_z - \sqrt{\tfrac{1}{6}}d_{xz} \pm \sqrt{\tfrac{1}{2}}d_{yz}$$

These functions are odd on reflection in the xy plane and are concentrated in lobes pointing along the three trigonal directions. They are called *strong* π-bonding orbitals because they require none of the atomic functions already used to form the σ bonds. It is also possible to form *weak* π bonds of the 1, 2, 3 type (even on reflection in the xy plane) from the E' functions (p_x, p_y) or $(d_{xy}, d_{x^2-y^2})$. These are weak because the E' functions are likely to be already partially used up in forming the σ bonds.

Working in the way shown in these examples, one can prepare an exhaustive table of the electronic configurations which are consistent with various bond symmetries. Such a table is given in the book of Eyring, Walter, and Kimball.[1] Group theory is incapable of deciding which of the various *possible* configurations will have the lowest energy and will therefore be found in nature. This must be decided by rules like Pauling's bond-strength criterion or by detailed calculations considering actual matrix elements of the Hamiltonian. However, the group theory *does* give considerable guidance in setting up functions of suitable symmetry to serve as a point of departure for detailed calculations.

EXERCISES

4-1 According to what irreducible representation of O does $xyzf(r)$ transform? Explain.

4-2 (*a*) Calculate the crystal-field potential up through terms of fourth degree resulting from point charges $-e$ located at $x = \pm a$, $y = \pm b$, and $z = \pm c$.

(*b*) Show that this may be written as a sum of six independent terms: a constant term, two homogeneous second-degree polynomials, and three homogeneous fourth-degree polynomials, each satisfying Laplace's equation $\nabla^2\varphi = 0$, and each invariant under the symmetry operations of the group D_{2h}. What are the coefficients in terms of a, b, and c? [HINT: Note that $r^l Y_l^m(\theta, \varphi)$ satisfies Laplace's equation; and verify that $(Y_l^m + Y_l^{-m})$, with l and m even integers, has th symmetry of D_{2h}.]

(*c*) Specialize your results for the cases $a = b \neq c$ (tetragonal field) an $a = b = c$ (cubic field).

4-3 The splitting of terms of $L = 0, 1, 2$, and 3 under a crystal-field perturbation of octahedral symmetry is given in the text. Determine the further splittin of each term under a small added perturbation having the symmetry group D (tetragonal group). You may assume that the D_4 axis coincides with one of th fourfold axes of the group O. The case $a = b \neq c$ above is an example of suc a field, but make the calculation purely group theoretically so that it is independ of the approximations of this model.

4-4 (*a*) Work out the character table of the tetragonal double group.

(*b*) Use it to determine the additional splitting of the levels of Exercise 4-3 the atom has an electronic spin of $\frac{3}{2}$ and the spin-orbit coupling is taken into accoun

4-5 Using the results of Exercise 3-11, work out the selection rules for magnet dipole transitions between the various irreducible representations of O and found in Exercise 4-3.

4-6 (*a*) According to what irreducible representation of O does H' $Ax^2 + By^2 - (A + B)z^2$ transform?

(*b*) If one considered this rhombic field as a perturbation applied to a situat of cubic symmetry, what sorts of matrix elements are allowed by symmetry?

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[1] H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry," p. 231, J. Wiley Sons, Inc., New York, 1944; see also G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940); J. H. Van Vleck and A. Sherman, *Revs. Mod. Phys.*, **7**, 174 (1935).

4-7 According to what irreducible representation of O_h does $z(x^2 - y^2)$ transform? What are its partners?

4-8 (*a*) What representations of D_{4h} are required to form four equivalent σ bonds directed from a central atom toward four others at the corners of a square?

(*b*) What electronic configurations using only $s, p,$ and d orbitals will form such hybrids?

(*c*) Find explicitly a set of four equivalent sp^2d hybrid σ bonds.

REFERENCES

BALLHAUSEN, C. J.: "Introduction to Ligand Field Theory," McGraw-Hill Book Company, Inc., New York, 1962.

BELL, DOROTHY G.: Group Theory and Crystal Lattices, *Revs. Modern Phys.*, **26,** 106 (1954).

BETHE, H. A.: Termaufspaltung in Kristallen, *Ann. Physik*, **3,** 133 (1929).

BUERGER, M. J.: "Elementary Crystallography," John Wiley & Sons, Inc., New York, 1956.

EYRING, H., J. WALTER, and G. E. KIMBALL: "Quantum Chemistry," app. VII, John Wiley & Sons, Inc., New York, 1944.

FICK, E.: Die Termaufspaltung in elektrostatischen Kristallfeldern, *Z. Physik*, **147,** 307 (1957).

KOSTER, G. F.: Space Groups and Their Representations, "Solid State Physics," vol. 5, p. 174, Academic Press Inc., New York, 1957.

LANDAU, L. D., and E. M. LIFSHITZ: "Quantum Mechanics, Non-relativistic Theory," chap. XII, Addison-Wesley Publishing Company, Inc., Reading, Mass., 1958.

OPECHOWSKI, W.: Sur les groupes cristallographiques "doubles," *Physica*, **7,** 552 (1940).

PHILLIPS, F. C.: "An Introduction to Crystallography," Longmans Green & Co., Inc., New York, 1946.

ROSENTHAL, JENNY E., and G. M. MURPHY: Group Theory and the Vibrations of Polyatomic Molecules, *Revs. Modern Phys.*, **8,** 317 (1936).

5 FULL ROTATION GROUP AND ANGULAR MOMENTUM

5-1 Rotational Transformation Properties and Angular Momentum

Before developing the representations of the full three-dimensional rotation group, let us review the underlying relation between the rotational transformation properties of a wavefunction and its angular momentum.

The *linear* momentum **p** of a system may be defined most basically as that quantity whose conservation is a consequence of the translational isotropy of space. Now, the isotropy of space means that the spatial gradient of the Hamiltonian H is zero and hence that ∇ commutes with H. But commutation of an operator with H is the requirement for conservation of that operator in quantum mechanics. Hence we associate ∇ with **p** and are led to the usual Schrodinger operator replacement $\mathbf{p} = (\hbar/i)\nabla$.

Considering for simplicity only the x component, we have

$$p_x\psi = \frac{\hbar}{i}\frac{\partial\psi}{\partial x} = \lim_{\delta x\to 0}\frac{\hbar}{i}\frac{\psi(x)-\psi(x-\delta x)}{\delta x}$$

$$= \lim_{\delta x\to 0} i\hbar\frac{P_{\delta x}-1}{\delta x}\psi(x)$$

where $P_{\delta x}$ is the transformation operator which shifts the contours of $\psi(x)$ by δx with respect to fixed axes (or shifts the axes by $-\delta x$ if the function is considered to be stationary). An alternative way of writing this equation is

$$P_{\delta x} = 1 - \frac{i(\delta x)p_x}{\hbar}$$

where δx is treated as infinitesimal. These equations state the relationship between the linear-momentum operator and the transformation operator $P_{\delta x}$ for translational displacement.

In a similar manner, we may *define* the x component of the *angular* momentum as the operator whose conservation follows from the invariance of the Hamiltonian under rotations about the x axis, i.e., from $\partial H/\partial\theta_x = 0$. In complete analogy to the linear momentum, we then obtain a definition of angular momentum in terms of infinitesimal rotations,

$$J_x\psi = \lim_{\delta\theta_x\to 0} i\hbar\frac{P_{\delta\theta_x}-1}{\delta\theta_x}\psi \tag{5-1}$$

or

$$P_{\delta\theta_x} = 1 - \frac{i(\delta\theta_x)}{\hbar}J_x \tag{5-2}$$

where $P_{\delta\theta_x}$ is the transformation operator which rotates the contours of the function by $\delta\theta_x$ about the x axis in the sense which makes a right-hand-screw advance along x. From this definition we can readily find the transformation operator P_{θ_x} for a finite rotation as follows: Let $\theta_x = n(\delta\theta_x)$, and let $n\to\infty$ while $(\delta\theta_x)\to 0$ in such a way as to hold θ_x constant. Then we can write P_{θ_x} as the result of $n = \theta_x/\delta\theta_x$ iterations of $P_{\delta\theta_x}$,

$$P_{\theta_x}\psi = \lim_{\delta\theta_x\to 0}(P_{\delta\theta_x})^{\theta_x/\delta\theta_x}\psi$$

$$= \lim_{\delta\theta_x\to 0}\left[1 - \frac{i(\delta\theta_x)}{\hbar}J_x\right]^{\theta_x/\delta\theta_x}\psi$$

$$= e^{-i\theta_x J_x/\hbar}\psi \tag{5-3a}$$

or

$$P_{\theta_x}\psi = \sum_{k=1}^{\infty}\frac{(-i\theta_x J_x/\hbar)^k}{k!}\psi \tag{5-3b}$$

where we have used the definition of the exponential e^y as the limit of $(1 + x)^{y/x}$ as $x \to 0$. The second form (5-3*b*) indicates how one could go about calculation with an exponential operator by Taylor's-series expansion. Clearly a result analogous to (5-3) is true for rotations about any axis, since we have made no special assumptions about the *x* axis. We have already made use of this result for the *z* component of the angular momentum in Sec. 4-4 while working out the character of the representations based on the spherical harmonics. Since the *z* axis was chosen for the axis of quantization, J_z had a definite value $m\hbar$ and we simply found

$$P_{\theta_z}\psi_m^{(j)} = e^{-im\theta_z}\psi_m^{(j)} \tag{5-4}$$

Note that this result follows directly from the relation between J_z and infinitesimal rotations. Hence it is valid whenever J_z is quantized. In particular, it holds also for half-integral *j* values where the spherical harmonics no longer serve as basis functions. This observation justifies our use of the formula (4-11) for the character $\chi_j(\alpha)$ for half-integral as well as integral values of *j*. The double-valued characters noted there are consequences of the fact that, for *half-integral j* values, $P_{2\pi}\psi_m^{(j)} = -\psi_m^{(j)}$, so that a rotation by 2π leaves the wavefunctions changed in phase.

We can use (5-3) to define the transformation operator for an arbitrary rotation about an arbitrary axis. In many applications, however, it is convenient to express the arbitrary rotation as a sequence of rotations about, say, the *x*, *y*, and *z* axes. In this case we simply operate successively with several operators of the type (5-3). For example, if the desired rotation θ can be carried out by a rotation by θ_y about the *y* axis followed by a rotation by θ_x about the *x* axis, we have

$$\begin{aligned} P_\theta\psi &= P_{\theta_x}P_{\theta_y}\psi \\ &= e^{-i\theta_xJ_x/\hbar}e^{-i\theta_yJ_y/\hbar}\psi \end{aligned}$$

Now, finite rotations do not in general commute. In fact, geometric inspection (Fig. 5-1) shows that, if one made the above rotations in the opposite order, one would need to perform a further rotation of magnitude $\theta_x\theta_y$ about the *z* axis to reach the same final position. (This statement is valid only to order θ^2, on the assumption that θ_x and θ_y are small.) In other words, to second order,

$$P_{\theta_x}P_{\theta_y} = P_{(\theta_x\theta_y)_z}P_{\theta_y}P_{\theta_x}$$

or

$$e^{-i\theta_xJ_x/\hbar}e^{-i\theta_yJ_y/\hbar} = e^{-i\theta_x\theta_yJ_z/\hbar}e^{-i\theta_yJ_y/\hbar}e^{-i\theta_xJ_x/\hbar}$$

If we now expand the exponentials to second order in the θ's, we find identical equality for the constant and linear terms. However, preserving the order and canceling identical terms, we obtain the requirement

$$\frac{-\theta_x\theta_yJ_xJ_y}{\hbar^2} = \frac{-i\theta_x\theta_yJ_z}{\hbar} - \frac{\theta_y\theta_xJ_yJ_x}{\hbar^2}$$

from the second-order terms. Upon canceling common factors, this becomes

$$J_xJ_y - J_yJ_x = i\hbar J_z \tag{5-5}$$

Thus the familiar commutation relations of the angular-momentum operators are seen to form the condition which must be satisfied if the transformation operator associated with a rotation about both x and y is to be uniquely defined regardless of the path by which the total rotation is accomplished.

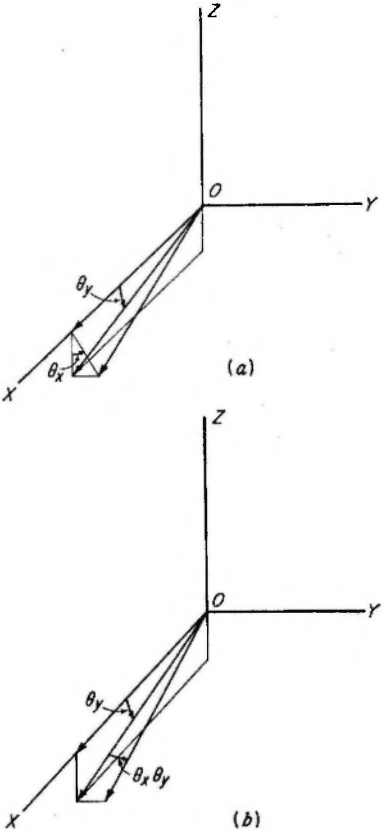

Fig. 5-1. *Illustration of noncommutativity of finite rotations. (a) shows $P_{\theta_x} P_{\theta_y}$ acting on a vector lying along the x axis; (b) shows that $P_{(\theta_x\theta_y)_z} P_{\theta_y} P_{\theta_x}$ yields the same result to second order in the angles. [It is characteristic of this simple illustrative example that P_{θ_x} has no effect in (b). The resulting equivalence is generally valid, however.]*

We may generalize from this example to obtain the other two angular-momentum commutation relations by cyclic interchange of x, y, and z. The three commutation relations obtained in this way completely determine the properties of the angular-momentum operators, and these operators may in fact be defined directly in this way. Purely algebraic development from the commutation relations has been used almost exclusively by Condon and Shortley,[1] and more recently by Racah and others, to deduce many properties of quantum-mechanical systems. However, in our group-theoretical development the emphasis is entirely on the transformation properties. In that framework, the commutation relations serve as the *integrability conditions* relating the transformation operators associated with the various rotations in such a way that the overall transformation associated with any finite rotation is uniquely determined regardless of the path by which it is carried out by integrating a sequence of infinitesimal rotations.

5-2 Continuous Groups

An infinite group is one containing an infinite number of elements. In most cases the individual elements will be specified by giving the values of one or more parameters p_i; for example, the three Eulerian angles specifying an arbitrary rotation from the full three-dimensional rotation group. In such a case, when all the group elements may be obtained by continuous variation of the parameters, the group is said to be *continuous*. Neighboring or adjacent group elements are those which differ by only small amounts in the values of all the parameters. We can also consider *mixed continuous* groups in which all group elements lie in a finite number of regions, within each of which all elements may be obtained by continuous variation of parameters. An example of a mixed continuous group is the rotation-inversion group in which the proper and improper rotations form two separate regions in group-element space.

If we confine our group elements to those which neighbor the identity, we have an *infinitesimal group*. Such groups were studied extensively by Lie and are often called *Lie groups*. All such groups are Abelian to the first order of infinitesimals. This may be readily seen by considering a matrix representation,

$$(\mathbf{E} + \epsilon\mathbf{A})(\mathbf{E} + \epsilon\mathbf{B}) = \mathbf{E} + \epsilon(\mathbf{A} + \mathbf{B}) + \epsilon^2\mathbf{AB}$$

$$(\mathbf{E} + \epsilon\mathbf{B})(\mathbf{E} + \epsilon\mathbf{A}) = \mathbf{E} + \epsilon(\mathbf{B} + \mathbf{A}) + \epsilon^2\mathbf{BA}$$

and recalling that matrix *addition* is always commutative. The noncommutativity of multiplication of matrices other than the unit matrix enters only in the second order of infinitesimals. Obviously the infinitesimal rotations form a Lie group.

The Hurwitz invariant integral. In developing the theory of finite groups we made heavy use of the rearrangement theorem. This theorem states that, as R runs over all the elements of the group, SR also runs over all elements, including each just once. From this we concluded that

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[1] E. U. Condon and G. H. Shortley, "Theory of Atomic Spectra," Cambridge University Press, New York, 1935.

$$\sum_R J(R) = \sum_R J(SR) \tag{5-6}$$

where $J(R)$ is any quantity depending only upon the element R. This statement was central to the proof of the orthogonality theorems on which most of our formal structure rests. When we consider continuous groups, we naturally convert such a sum to an integral over the parameters which specify the group elements. The simple proof given for the finite groups fails, however, because one cannot set up a simple correspondence of one element to another. Rather, one can only deal with a density of group elements in a region defined by certain values of the parameters. Then one obtains a so-called "Hurwitz integral" of the sort

$$\begin{aligned}\sum_R J(R) \to \int J(R)\,dR &= \int J(R)g(R)\,dp_1\cdots dp_n \\ &= \int J(R\{p_1,\ldots,p_n\})g(R\{p_1,\ldots,p_n\})\,dp_1\cdots dp_n\end{aligned} \tag{5-7}$$

where $R\{p_1,\ldots,p_n\}$ is the group element fixed by the parameter values $p_1,\ldots,p_n$ and $g(R)$ is the density of group elements in the parameter space in the neighborhood of R. The desired result is now that

$$\int J(SR)\,dR = \int J(R)\,dR \tag{5-8}$$

This will hold provided that the density of group elements R_i in group space is such that the density of points SR_i will always be the same as that of the points R_i. The problem is to find a suitable $g(R)$ to convert the integral into one which can actually be carried out explicitly in parameter space. Since there is always an arbitrary normalization factor in the desired invariant density in parameter space $g(R)$, it is convenient to normalize to g_0, the density in the neighborhood of the identity. We may then obtain the desired $g(R)$ by noting that R takes each group element from a volume element V_0 near E to a new element in a volume V near R. This volume is determined by simply operating with R on all elements in V_0, as illustrated in Fig. 5-2. Since we have the same number of points in each volume, we have

$$g(R) = \frac{g_0 V_0}{V} \tag{5-9}$$

and $g(R)$ is determined by the contraction of the volume element V_0 as it is moved from E to R. This contraction is given by the Jacobian of the transformation associated with R, namely,

$$g(R) = g_0 \left\{ \frac{\partial[p_1(RE\{e_1, \ldots, e_n\}), \ldots, p_n(RE\{e_1, \ldots, e_n\})]}{\partial[e_1, \ldots, e_n]} \right\}^{-1} \qquad (5\text{-}10)$$

where the derivatives in the Jacobian are to be evaluated at the values of the parameters $e_i = p_i(E)$ corresponding to the identity.

The actual calculation of the density function from (5-10) is usually laborious. However, as soon as it is seen that such an invariant density exists, it follows that all the orthogonality theorems carry over to the case of continuous groups. The proper weighting functions $g(R)$ for a given parametrization can then be found by elementary means. In any case, we have the orthogonality theorem

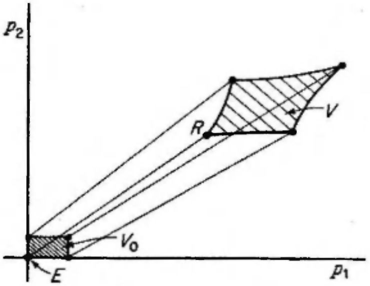

Fig. 5-2. *Illustration of transformation of group elements in V_0 at E into those in V at R in a two-dimensional parameter space.*

$$\int \Gamma^{(j)}(R)^*_{\kappa\lambda}\Gamma^{(j')}(R)_{\kappa'\lambda'}\, dR = \frac{\delta_{jj'}\delta_{\kappa\kappa'}\delta_{\lambda\lambda'}}{l_j}\int dR \qquad (5\text{-}11)$$

where l_j is the dimensionality of the representation $\Gamma^{(j)}$ and $\int dR$ depends upon the normalization choice for $g(R)$. The corresponding result for the orthogonality of the characters is

$$\int \chi^{(j)}(R)^*\chi^{(j')}(R)\, dR = \delta_{jj'}\int dR \qquad (5\text{-}12)$$

As an example of how (5-12) can be carried out in practice, we consider the character for rotations which we worked out earlier, namely,

$$\chi^{(j)}(\alpha) = \frac{\sin(j + \frac{1}{2})\alpha}{\sin(\alpha/2)}$$

This is the character for all elements in the class of rotations by α, regardless of the axis of rotation. Thus we need a new kind of density function $g'(\alpha)$

which includes the effect of integrating $g(R)$ over all possible Eulerian angles, for example, which are consistent with an overall rotation by α. This would be hard to compute using (5-10). However, if we know that (5-12) must be valid, we may proceed to infer $g'(\alpha)$. Thus, we require

$$\int_0^{2\pi} \frac{\sin[(j+\frac{1}{2})\alpha]\sin[(j'+\frac{1}{2})\alpha]g'(\alpha)\,d\alpha}{\sin^2(\alpha/2)}$$

$$= \int_0^{2\pi} [\cos(j-j')\alpha - \cos(j+j'+1)\alpha]\left[\frac{g'(\alpha)}{2\sin^2(\alpha/2)}\right] d\alpha$$

$$= \delta_{jj'}\int_0^{2\pi} g'(\alpha)\,d\alpha$$

Since the cosine terms will integrate to $\delta_{jj'}$ if multiplied only by a constant, we are led to take $g'(\alpha) \sim \sin^2(\alpha/2)$. This is a reasonable form since the solid angle into which rotations by angles between α and $\alpha + d\alpha$ can be made goes to zero as $\alpha \to 0$ and as $\alpha \to 2\pi$. Such arguments are obviously not rigorous, but at least the result is plausible.

5-3 Representation of Rotations through Eulerian Angles

The most convenient manner of expressing an arbitrary rotation of axes is by the three Eulerian angles. We follow Rose's convention[1] and define the angles as follows. Starting with an x, y, z coordinate system, rotate by α about the z axis, and denote the new axes x', y', z'. Then rotate by β about the y' axis, and denote the resulting axes x'', y'', z''. Finally rotate by γ about the z'' axis, and label the final axes x''', y''', z'''. These rotations are illustrated in Fig. 5-3. Note that the successive rotations here are made about *rotated* axes, not the set x, y, z of space-fixed axes. Since it is often convenient to consider all rotations with respect to a permanent set of space-fixed axes, we now note that the same final rotated axes x''', y''', z''' could have been obtained by carrying out the rotations in reverse order about fixed axes. That is, we could have rotated by γ about z, then by β about y, and finally by α about z again. This equivalence is readily verified by considering some examples of successive finite rotations. It can also be proved rigorously by considerations of the sort used in discussing the elements conjugate to each other in a class. Consider first a simple case where $\gamma = 0$. Then we have only two rotations to consider, and we wish to establish the equality

$$P_z(\alpha)P_y(\beta) = P_{y'}(\beta)P_z(\alpha)$$

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[1] M. E. Rose, "Elementary Theory of Angular Momentum," chap. IV, J. Wiley & Sons, Inc., New York, 1957.

where $P_i(\theta)$ represents a rotational transformation about the ith axis by θ. But this is the same as requiring that

$$P_y(\beta) = P_z^{-1}(\alpha)P_{y'}(\beta)P_z(\alpha)$$

In this form, the statement is that $P_y(\beta)$ is the same rotation as could be accomplished by first using $P_z(\alpha)$ to move the y axis into the y' position, performing a rotation $P_{y'}(\beta)$ about it there, and then using $P_z^{-1}(\alpha)$ to return the y axis to its normal position. In a similar way, one can see that

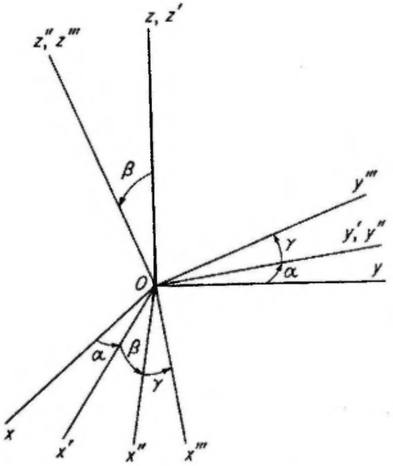


Fig. 5-3. *The Eulerian angles.*

$$P_z(\gamma) = P_z^{-1}(\alpha)P_{y'}^{-1}(\beta)P_{z''}(\gamma)P_{y'}(\beta)P_z(\alpha)$$

Combining this with the above results shows that

$$P_z(\alpha)P_y(\beta)P_z(\gamma) = P_{z''}(\gamma)P_{y'}(\beta)P_z(\alpha) \tag{5-13}$$

and we can accomplish the desired rotation always using fixed axes. The actual operator is then simply

$$P(\alpha, \beta, \gamma) = P_z(\alpha)P_y(\beta)P_z(\gamma) = e^{-i\alpha J_z/\hbar}e^{-i\beta J_y/\hbar}e^{-i\gamma J_z/\hbar} \tag{5-14}$$

What we now seek are the matrices $D^{(j)}(\alpha, \beta, \gamma)_{m'm}$ which describe how the angular-momentum eigenfunctions of angular momentum j and z component m (in units of $\hbar$) transform under the general rotation operator (5-14). Let us denote one of these eigenfunctions by $\varphi_m^{(j)}$. (If j is integral, these transform simply as the spherical harmonics.) Then by definition of the representation matrices

$$P(\alpha, \beta, \gamma)\varphi_m^{(j)} = \sum_{m'} \varphi_{m'}^{(j)} D^{(j)}(\alpha, \beta, \gamma)_{m'm} \tag{5-15}$$

Because of our choice of z-axis quantization, J_z is a diagonal operator, and the effect of the rotations by α and γ is easily written by using the exponential form of the rotation operator. However, the rotation $P_y(\beta)$ will have a nondiagonal representation, which we denote $\mathbf{d}^{(j)}(\beta)$. Combining the three, we find

$$P(\alpha, \beta, \gamma)\varphi_m^{(j)} = \sum_{m'} \varphi_{m'}^{(j)} e^{-im'\alpha} d^{(j)}(\beta)_{m'm} e^{-im\gamma} \tag{5-16}$$

or

$$D^{(j)}(\alpha, \beta, \gamma)_{m'm} = e^{-im'\alpha} d^{(j)}(\beta)_{m'm} e^{-im\gamma} \tag{5-17}$$

Thus the problem of finding the representation matrices of the full rotation group has been reduced to that of finding $\mathbf{d}^{(j)}(\beta)$. These matrices will now be determined for arbitrary integral or half-integral angular momentum j by an indirect procedure due to H. Weyl, which utilizes the homomorphism between the group of three-dimensional rotations and the group of 2 × 2 unitary matrices with determinant 1.

5-4 Homomorphism with the Unitary Group

It is apparent that the set of all 2 × 2 unitary matrices with determinant +1 forms a group, since it is closed under multiplication, it has a unit element, and it has an inverse for each element. The most general matrix in this group may be written as

$$\mathbf{u} = \begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix} \tag{5-18}$$

with the subsidiary condition $aa^* + bb^* = |a|^2 + |b|^2 = 1$ following from the requirement that the determinant be $+1$. Since a and b are in general complex, this leaves three independent parameters, which we shall presently relate to the three Eulerian angles.

To do this, we introduce the three Pauli matrices, which in the phase convention of Condon and Shortley take the form

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{5-19}$$

Evidently, we can express *any* 2 × 2 matrix with vanishing trace as a linear combination of these three. Denoting the coefficient of σ_x by x, etc., we have, for the general matrix $\mathbf{h}$,

$$\mathbf{h} = \begin{pmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{pmatrix} = x\sigma_x + y\sigma_y + z\sigma_z \equiv \mathbf{r} \cdot \boldsymbol{\sigma} = \begin{pmatrix} z & x - iy \\ x + iy & -z \end{pmatrix} \tag{5-20}$$

Solving for the coefficients x, y, z, we find

$$x = \frac{h_{21} + h_{12}}{2} \qquad y = \frac{h_{21} - h_{12}}{2i} \qquad z = h_{11} = -h_{22} \tag{5-21}$$

We also note that, if x, y, and z are real, then $\mathbf{h}$ is Hermitian.

Now let us transform $\mathbf{h}$ into a new matrix $\mathbf{h}'$ by a unitary transformation using a matrix $\mathbf{u}$ from the 2×2 unitary group. Then

$$\mathbf{h}' = \mathbf{u}\mathbf{h}\mathbf{u}^{-1} = \mathbf{r}' \cdot \boldsymbol{\sigma} \tag{5-22}$$

defines a new set of coordinates x', y', z' related to the first set x, y, z. If we carry out explicitly the matrix multiplication indicated in (5-22), using the definitions (5-18) and (5-20), we find

$$\begin{aligned} x' &= \frac{h'_{21} + h'_{12}}{2} \\ &= \frac{1}{2}(a^2 + a^{*2} - b^2 - b^{*2})x \\ &\qquad + \frac{i}{2}(-a^2 + a^{*2} - b^2 + b^{*2})y - (ab + a^*b^*)z \\ y' &= \frac{h'_{21} - h'_{12}}{2i} \\ &= \frac{i}{2}(a^2 - a^{*2} + b^{*2} - b^2)x \\ &\qquad + \frac{1}{2}(a^2 + a^{*2} + b^2 + b^{*2})y + i(a^*b^* - ab)z \\ z' &= h'_{11} = -h'_{22} = (a^*b + ab^*)x \\ &\qquad + i(a^*b - ab^*)y + (aa^* - bb^*)z \end{aligned} \tag{5-23}$$

Thus, *associated with each* 2×2 *matrix* $\mathbf{u}$ *there is a* 3×3 *matrix* $\mathbf{R}(\mathbf{u})$ *which transforms* x, y, z *into* x', y', z'. The elements of $\mathbf{R}(\mathbf{u})$ may be read out from (5-23), which can be expressed more compactly as

$$\mathbf{r}' = \mathbf{R}(\mathbf{u})\mathbf{r} \tag{5-24}$$

or, in terms of components, $r'_i = \sum_j [\mathbf{R}(\mathbf{u})]_{ij} r_j$.

We can see that $\mathbf{R}(\mathbf{u})$ actually represents a simple rotation of coordinates by making several observations. First, $\mathbf{R}(\mathbf{u})$ is real, as is evident from inspection of the elements displayed in (5-23). Second, we note that lengths are preserved since

$$|h'| = |u| \cdot |h| \cdot |u^{-1}| = |h|$$

and $\quad |h| = -z^2 - (x + iy)(x - iy) = -(x^2 + y^2 + z^2)$

Thus $\quad x^2 + y^2 + z^2 = x'^2 + y'^2 + z'^2$

But if lengths are preserved, all angles must be also and the transformation must be either a proper or an improper rotation. The inversion is excluded, however, since all elements may be obtained by continuous variation of the parameters (a, b) in $\mathbf{u}$ from the values $(1, 0)$ which yield the identity transformation. Hence the determinant of $\mathbf{R}(\mathbf{u})$ must be $+1$ for all values of the parameters, since there is no way for it to jump discontinuously to -1. Therefore we may conclude that $\mathbf{R}(\mathbf{u})$ *is a real orthogonal matrix representing a proper rotation of coordinates.*

Explicit relation between u and R(u). If we choose $\mathbf{u}$ to be diagonal, its most general form is

$$\mathbf{u}_1(\alpha) = \begin{pmatrix} e^{i\alpha/2} & 0 \\ 0 & e^{-i\alpha/2} \end{pmatrix} \tag{5-25a}$$

By using the general formula (5-23), this leads to the matrix

$$R_1(\alpha) = \begin{pmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{5-25b}$$

which is precisely the rotation matrix for a rotation of coordinates by an angle α about z.

If instead we choose $\mathbf{u}$ to be real, the most general form is

$$\mathbf{u}_2(\beta) = \begin{pmatrix} \cos\dfrac{\beta}{2} & \sin\dfrac{\beta}{2} \\ -\sin\dfrac{\beta}{2} & \cos\dfrac{\beta}{2} \end{pmatrix} \tag{5-26a}$$

This produces the rotation matrix

$$R_2(\beta) = \begin{pmatrix} \cos\beta & 0 & -\sin\beta \\ 0 & 1 & 0 \\ \sin\beta & 0 & \cos\beta \end{pmatrix} \tag{5-26b}$$

which describes a rotation through β about the y axis.

With these two components, we can express the rotation of coordinates through an arbitrary set of Eulerian angles by the product matrix

$$\mathbf{u}(\alpha, \beta, \gamma) = \mathbf{u}_1(\gamma)\mathbf{u}_2(\beta)\mathbf{u}_1(\alpha)$$

If we carry out the indicated multiplications, we obtain

$$\mathbf{u}(\alpha, \beta, \gamma) = \begin{pmatrix} e^{i(\alpha+\gamma)/2}\cos\dfrac{\beta}{2} & e^{i(\gamma-\alpha)/2}\sin\dfrac{\beta}{2} \\ -e^{-i(\gamma-\alpha)/2}\sin\dfrac{\beta}{2} & e^{-i(\alpha+\gamma)/2}\cos\dfrac{\beta}{2} \end{pmatrix} \tag{5-27}$$

Thus we have proved that *an arbitrary rotation can be induced by a suitable matrix from the unitary group.* However, we shall now show that the matrix $-\mathbf{u}$ represents the same rotation, so that the representation is not unique, but "double-valued."

This ambiguity of sign arises from the defining relation $\mathbf{h}' = \mathbf{u}\mathbf{h}\mathbf{u}^{-1}$. Since this is quadratic in $\mathbf{u}$, the resulting $\mathbf{h}'$ is unchanged by a uniform sign change in $\mathbf{u}$ (which changes the sign of $\mathbf{u}^{-1}$ also). Another evidence of the ambiguity is the appearance of half angles in (5-27). Since the Eulerian angles specifying a rotation are determined only within multiples of 2π, the half angles are determined only within π. But all trigonometric functions and complex exponentials change sign when the argument is changed by π. Therefore the sign of the matrix $\mathbf{u}$ suffers an ambiguity.

We conclude: *there is a two-fold homomorphism between the group of* 2×2 *unitary matrices with* $|\mathbf{u}| = 1$ *and the group of three-dimensional pure rotations. The two matrices* $\mathbf{u}$, $-\mathbf{u}$ *are associated with a rotation* $\mathrm{R}(\mathbf{u})$, *and we have formulas establishing the relation in either direction.* Having established this homomorphism, we now work out all the representations of the unitary group by a simple method. Because of the homomorphism, these same matrices will serve as the representation matrices for the three-dimensional rotation group.

5-5 Representations of the Unitary Group

Clearly the matrices $\mathbf{u}$ themselves form a two-dimensional representation of the group. We may denote the two basis functions by ξ_1 and ξ_2, so that by definition

$$\xi_i' = P(\mathbf{u})\xi_i = \sum_{j=1}^{2} \xi_j u_{ji} \tag{5-28a}$$

or, written out fully,

$$(\xi_1', \xi_2') = (a\xi_1 - b^*\xi_2, b\xi_1 + a^*\xi_2) \tag{5-28b}$$

Starting with (5-28), we can generate representations of higher dimensionality by taking the basis functions to be the $(n + 1)$ monomials of degree n, namely, $f_p'^{(n)} = \xi_1^p \xi_2^{n-p}$. In that case, we have

$$\begin{aligned} P(\mathbf{u}) f_p'^{(n)}(\xi_1, \xi_2) &= f_p'^{(n)}(\xi_1', \xi_2') = (a\xi_1 - b^*\xi_2)^p (b\xi_1 + a^*\xi_2)^{n-p} \\ &= \sum_{p'} f_{p'}'^{(n)} U'^{(n)}(\mathbf{u})_{p'p} \end{aligned}$$

and the last equality can be written because the polynomial in the previous step is homogeneous of degree n. Thus the $f_p'^{(n)}$ do form a basis for an $(n + 1)$-dimensional representation $\mathrm{U}'^{(n)}$ of $\mathbf{u}$. It is not unitary as it stands, however, except for $n = 1$. To make it unitary, we must insert a normalizing factor $\sqrt{p!\,(n-p)!}$ in the denominator of $f_p'^{(n)}$, and we denote the normalized function simply $f_p^{(n)}$. This normalization factor will be justified shortly. Also, to prepare for the connection with the rotation group, we now change notation by setting

$$n = 2j \qquad p = j + m$$

The normalized basis functions are then given by the symmetrical form

$$f_m^{(j)} = \frac{\xi_1^{\,j+m}\xi_2^{\,j-m}}{\sqrt{(j+m)!\,(j-m)!}} \qquad m = -j, \ldots, j-1, j \tag{5-29}$$

We may now work out the unitary-representation matrices $U_{m'm}^{(j)}$ explicitly by simply using the binomial expansion. Thus

$$P(\mathbf{u})f_m^{(j)} = \frac{(a\xi_1 - b^*\xi_2)^{j+m}(b\xi_1 + a^*\xi_2)^{j-m}}{\sqrt{(j+m)!\,(j-m)!}}$$

$$= \sum_\kappa \frac{(a\xi_1)^{j+m-\kappa}(-b^*\xi_2)^\kappa (j+m)!}{\sqrt{(j+m)!}\,\kappa!\,(j+m-\kappa)!} \sum_{\kappa'} \frac{(b\xi_1)^{j-m-\kappa'}(a^*\xi_2)^{\kappa'}(j-m)!}{\sqrt{(j-m)!}\,(j-m-\kappa)!\,\kappa'!}$$

Note that the general term contains $\xi_1^{\,2j-(\kappa+\kappa')}\xi_2^{\kappa+\kappa'} \sim f_{j-\kappa-\kappa'}^{(j)}$. Thus, if we set $\kappa' = j - m' - \kappa$, this is the $f_{m'}^{(j)}$ term in the sum. Eliminating the index κ' in favor of m', and collecting factors, we obtain

$$P(\mathbf{u})f_m^{(j)} = \sum_{m'} f_{m'}^{(j)} U^{(j)}(\mathbf{u})_{m'm} \tag{5-30a}$$

where

$$U^{(j)}(\mathbf{u})_{m'm} = \sum_\kappa \frac{(-1)^\kappa \sqrt{(j+m)!\,(j-m)!\,(j+m')!\,(j-m')!}}{\kappa!\,(j+m-\kappa)!\,(j-\kappa-m')!\,(\kappa+m'-m)!}$$

$$\times\ a^{j+m-\kappa}(a^*)^{j-\kappa-m'}b^{\kappa+m'-m}(b^*)^\kappa \tag{5-30b}$$

The summation runs over all values of κ for which the denominator is finite. For example, if $m' = j$, the denominator is infinite unless $\kappa = 0$. [This is so because the factorial of a negative integer is taken to be infinite, as follows from the relation between the factorial and gamma functions, namely, $n! = \Gamma(n+1)$.] Thus in this case there is only one term in the sum, and we find

$$U^{(j)}(\mathbf{u})_{jm} = \sqrt{\frac{(2j)!}{(j+m)!\,(j-m)!}}\, a^{j+m}b^{j-m} \tag{5-31}$$

The matrices defined in (5-30) *as j takes on all integral and half-integral values include all the distinct, irreducible, unitary representations of the two-dimensional unitary group.* We now set about verifying this statement.

First, we show that the factorial denominator in (5-29) is in fact the proper normalizing factor. We use the generalized Unsold theorem (Sec. 4-9), and consider the sum $\sum_m |f_m^{(j)}|^2$, which must be invariant if the $f_m^{(j)}$ are (normalized) basis functions for a unitary representation.

$$\sum_{m=-j}^{j} |f_m^{(j)}|^2 = \sum_m \frac{|\xi_1^2|^{j+m}\,|\xi_2^2|^{j-m}}{(j+m)!\,(j-m)!} = \frac{(|\xi_1^2| + |\xi_2^2|)^{2j}}{(2j)!}$$

where the last step follows by the binomial theorem. But $|\xi_1^2| + |\xi_2^2|$ is invariant under all the operations **u**, since ξ_1 and ξ_2 are by definition basis functions of a unitary representation, and so Unsold's theorem applies to them. But any power of an invariant is also invariant. Thus $\sum_m |f_m^{(j)}|^2$ is invariant as required. Evidently this would not have been true without the factorial denominator, which allowed the application of the binomial theorem.

Next we prove the *irreducibility* of these representations by use of Schur's lemma (Sec. 3-2). We start by restricting attention to diagonal matrices **u**. Then $b = 0$, $|a| = 1$, and we may set $a = e^{i\alpha/2}$. The only nonvanishing terms in (5-30) then arise when $\kappa = 0$ and $m' = m$. In this case (5-30*b*) simplifies to

$$U^{(j)}_{m'm}(\alpha) = \delta_{m'm}(e^{i\alpha/2})^{j+m}(e^{-i\alpha/2})^{j-m} = \delta_{m'm}e^{im\alpha} \qquad (5\text{-}32)$$

Now, following Schur's lemma, we assume that there exists a matrix **M** which commutes with *all* **U**, and hence certainly with all members of this restricted set. Then

$$\mathbf{MU} = \mathbf{UM}$$

$$M_{mm'}U_{m'm'} = U_{mm}M_{mm'}$$

$$M_{mm'}(e^{im\alpha} - e^{im'\alpha}) = 0$$

Therefore $M_{mm'} = 0$ for $m \neq m'$, and **M** must be diagonal. Now we consider a general matrix **u** which produces off-diagonal as well as diagonal terms in **U**, as is evident from (5-30*b*). Then **MU** = **UM** implies

$$M_{mm}U_{mm'} = U_{mm'}M_{m'm'}$$

and since $U_{mm'} \neq 0$ by hypothesis, $M_{mm} = M_{m'm'}$, and **M** must be not only diagonal but a constant matrix. From Schur's lemma it then follows that the matrices $\mathbf{U}^{(j)}$ form irreducible representations of the unitary group.

Finally, we show the *completeness* of this set of representations. This follows from the orthogonality of characters. We may restrict our attention to diagonal **u** since all **u** are in the same class with some diagonal **u**′ related to it by a unitary transformation. From (5-32), we have for a diagonal matrix

$$\chi^{(j)}(\alpha) = \sum_m U_{mm}{}^{(j)}(\alpha) = \sum_{m=-j}^{j} e^{im\alpha} \tag{5-33}$$

where now j can take on integral or half-integral values. Any other distinct representation would need to have a character orthogonal [with some suitable weighting function $g(\alpha)$] to all such $\chi^{(j)}$ and therefore to all $\chi^{(j)} - \chi^{(j-1)} = 2\cos j\alpha$. But since we now include half integral j as well as integral j, these functions form a complete set in the region from 0 to $\pm 2\pi$ over which α can roam in forming all distinct **u**. Thus no other representations are possible. Note that the half-integral j values are required to extend the region of completeness for a cosine series from $\pm\pi$ to $\pm 2\pi$.

5-6 Representation of the Rotation Group by Representations of the Unitary Group

Having worked out the homomorphism between the rotation group and the unitary group, and the complete set of irreducible representations of the latter, we can now write out the irreducible representations of the rotation group directly. The simplest one is the trivial case $\mathbf{U}^{(0)}(\mathbf{u}) = 1$, which corresponds to $\mathbf{D}^0(\alpha, \beta, \gamma) = 1$. This merely states that a quantum state with no angular momentum (an S state) is invariant under all rotations.

Next we have $\mathbf{U}^{(\frac{1}{2})}(\mathbf{u})$, which is just **u** itself. The **u** matrix which induces a coordinate transformation characterized by the Eulerian angles α, β, γ is given by (5-27). Hence (5-27) must be equivalent to the two-dimensional representation of the rotation group based on angular-momentum eigenfunctions for $j = \frac{1}{2}$. In fact, by working through the Pauli matrices, we have developed precisely the representation matrices based on $\varphi_{\frac{1}{2}}{}^{(\frac{1}{2})}$ and $\varphi_{-\frac{1}{2}}{}^{(\frac{1}{2})}$ for the first and second rows, respectively. Even the phases are conventional. Only one caution is required. We have developed the correspondence between $\mathbf{u}(\alpha, \beta, \gamma)$ and $\mathbf{R}[\mathbf{u}(\alpha, \beta, \gamma)]$ for positive rotations of *coordinate axes* about successively rotated axes. Thus, to represent positive rotations of the contours of the functions about fixed axes, which is our conventional interpretation, we must use

$$\mathbf{R}^{-1}[\mathbf{u}(\alpha, \beta, \gamma)] = \mathbf{R}[\mathbf{u}(-\gamma, -\beta, -\alpha)].$$

Accordingly, we obtain

$$\mathbf{D}^{(\frac{1}{2})}(\alpha, \beta, \gamma) = \begin{pmatrix} e^{-i(\alpha+\gamma)/2}\cos\frac{\beta}{2} & -e^{-i(\alpha-\gamma)/2}\sin\frac{\beta}{2} \\ e^{i(\alpha-\gamma)/2}\sin\frac{\beta}{2} & e^{i(\alpha+\gamma)/2}\cos\frac{\beta}{2} \end{pmatrix} \quad \blacktriangleright \quad (5\text{-}34)$$

This matrix tells how the two eigenfunctions of spin $\frac{1}{2}$ transform under an arbitrary rotation, specified by the Eulerian angles. As noted earlier, we see from (5-34) that one of these half-integral angular-momentum eigenfunctions transforms into its negative under a rotation by 2π in any direction, and we must consider rotations of 4π before we find the identity. These eigenfunctions are called *spinors* to distinguish their unusual rotational-transformation properties from those of vectors. If we accept this essential difference, we can consider (5-34) to form a single-valued representation for rotations up to 4π. This was the approach used in Sec. 4-7 in treating the crystal double groups. No physical nonsense can arise from the sign change under rotation by 2π, since all physically significant quantities are matrix elements of the sort

$$\int \psi_i^* F \psi_j \, d\tau$$

which will be unchanged by a simultaneous sign change in ψ_i and ψ_j. (The matrix element will be *zero* if one of the functions has half integral j and the other has integral j.)

We can obtain all the higher-dimensional representations of the rotation group by using the higher-dimensional representations (5-30) of the unitary group and the connection rule

$$\mathbf{D}^{(j)}(\alpha, \beta, \gamma) = \mathbf{U}^{(j)}[\mathbf{u}(-\gamma, -\beta, -\alpha)]$$

That is, we set

$$a = e^{-i(\alpha+\gamma)/2} \cos \frac{\beta}{2}$$

$$b = -e^{-i(\alpha-\gamma)/2} \sin \frac{\beta}{2}$$

in (5-30). If this is done, we obtain

$$D^{(j)}(\alpha, \beta, \gamma)_{m'm} = e^{-im'\alpha} e^{-im\gamma} \sum_{\kappa} \frac{(-1)^{\kappa} \sqrt{(j+m)!\,(j-m)!\,(j+m')!\,(j-m')!}}{\kappa!\,(j+m-\kappa)!\,(j-m'-\kappa)!\,(\kappa+m'-m)!} \times \left(\cos \frac{\beta}{2}\right)^{2j-2\kappa-m'+m} \left(-\sin \frac{\beta}{2}\right)^{2\kappa+m'-m} \quad ▶ \quad (5\text{-}35)$$

as the general expression for the representation of the transformation properties of angular-momentum eigenfunctions under rotation through the Eulerian angles.

We have already considered the special cases $\mathbf{D}^{(0)}$ and $\mathbf{D}^{(\frac{1}{2})}$. Now let us examine the explicit form for $j = 1$ which gives the transformation properties of p functions. Using the general formula (5-35), we find

$$\mathbf{D}^{(1)}(\alpha, \beta, \gamma) = \begin{bmatrix} e^{-i\alpha}\dfrac{1+\cos\beta}{2}e^{-i\gamma} & -e^{-i\alpha}\dfrac{\sin\beta}{\sqrt{2}} & e^{-i\alpha}\dfrac{1-\cos\beta}{2}e^{i\gamma} \\ \dfrac{\sin\beta}{\sqrt{2}}e^{-i\gamma} & \cos\beta & -\dfrac{\sin\beta}{\sqrt{2}}e^{i\gamma} \\ e^{i\alpha}\dfrac{1-\cos\beta}{2}e^{-i\gamma} & e^{i\alpha}\dfrac{\sin\beta}{\sqrt{2}} & e^{i\alpha}\dfrac{1+\cos\beta}{2}e^{i\gamma} \end{bmatrix}. \tag{5-36}$$

In this result we note that the half angles have all disappeared. This shows that $\mathbf{D}^{(1)}$ is invariant under rotations of 2π and hence is single-valued, as it should be for integral j. We can see that this property is general by inspecting the general form (5-30*b*). Going from $\mathbf{u}$ to $-\mathbf{u}$ introduces a factor

$$(-1)^{j+m-\kappa}(-1)^{j-\kappa-m'}(-1)^{\kappa+m'-m}(-1)^{\kappa} = (-1)^{2j}$$

into $\mathbf{U}^{(j)}$ and hence $\mathbf{D}^{(j)}$ but gives the same rotation of coordinates $\mathbf{R}(\mathbf{u})$. Thus, if j is half-integral, we have an ambiguity of sign but none appears if j is integral.

5-7 Application of the Rotation-representation Matrices

First, let us review the conventions about sense and order of the rotations under which the $\mathbf{D}^{(j)}(\alpha, \beta, \gamma)$ may be used. In all cases, we assume the Condon and Shortley phase convention for the angular-momentum eigenfunctions, namely, $\Theta_l^{|m|} = (-1)^m\Theta_l^{-|m|}$, so that $\varphi_{-m}^{(j)} = (-1)^m\varphi_m^{(j)*}$. We always assume right-handed coordinate systems, and rotations are considered positive if they are of the sense which would advance a right-hand screw in the positive direction along the axis. In these terms, the fundamental case for which the $D^{(j)}(\alpha, \beta, \gamma)$ were derived is that in which α, β, γ are positive rotations of the *functions* with respect to a permanently fixed coordinate system, with the rotation by γ being performed first. As we noted in Sec. 5-3, we could obtain the same rotation of a function if we imagined a coordinate system to be attached to it and then made successive rotations about these rotated axes in the reverse order, so that the α rotation was made first. Even in this case, though, the rotated function is still considered to be represented in terms of basis functions set up with respect to the permanent space-fixed axes.

An alternative view can be adopted, in which the function under operation is considered permanently *fixed* in space and the *axes* (and basis functions) are considered to be rotated. To apply our formulas to this viewpoint, we note that, if the same rotation were applied to both the axes and the function being transformed, clearly the relative position would be unchanged and so the transformation matrix would simply be the identity. That is,

$$\mathbf{D}^{(j)}_{\text{axes}}(\alpha, \beta, \gamma)\, \mathbf{D}^{(j)}_{\text{funct}}(\alpha, \beta, \gamma) = \mathbf{E}$$

Thus $$\mathbf{D}^{(j)}_{\text{funct}}(\alpha, \beta, \gamma) = \mathbf{D}^{(j)}_{\text{axes}}(\alpha, \beta, \gamma)^{-1} = \mathbf{D}^{(j)}_{\text{axes}}(-\gamma, -\beta, -\alpha)$$

That is, we can use the same $\mathbf{D}^{(j)}(\alpha, \beta, \gamma)$ in the second viewpoint to represent rotations of *axes* by $-\alpha$, $-\beta$, $-\gamma$ in the reverse order to that used if the function were being rotated. For example, if we rotated axes about space-fixed axes, we would have to make negative rotations by α, β, γ, with the α rotation being performed first.

The conclusions are summarized in Table 5-1.

Table 5-1

Eulerian-angle conventions

Rotated	*Sense*	*With respect to*	*Order of operators*
a. Function	+	Fixed axes	$P(\alpha)P(\beta)P(\gamma)$
b. Function	+	Rotated axes	$P(\gamma)P(\beta)P(\alpha)$
c. Axes	−	Fixed axes	$P(\gamma)P(\beta)P(\alpha)$
d. Axes	−	Rotated axes	$P(\alpha)P(\beta)P(\gamma)$

Application to combined basis functions. In many applications, such as to directed-valence orbitals, one is interested in knowing the effect of a rotation on some wavefunction which is a linear combination of several basis functions. In this case, if

$$\begin{aligned}
\psi &= \sum_m \varphi_m{}^{(j)} c_m = \boldsymbol{\varphi}^{(j)}\mathbf{c} \\
P(\alpha, \beta, \gamma)\psi &= \sum_m c_m P(\alpha, \beta, \gamma)\varphi_m{}^{(j)} \\
&= \sum_m c_m \sum_{m'} \varphi_{m'}{}^{(j)} D^{(j)}(\alpha, \beta, \gamma)_{m'm} \\
&= \sum_{m'} \varphi_{m'}{}^{(j)} [\mathbf{D}^{(j)}(\alpha, \beta, \gamma)\mathbf{c}]_{m'} = \boldsymbol{\varphi}^{(j)}\mathbf{c}'
\end{aligned} \tag{5-37}$$

where $\mathbf{c}$ is the column vector composed of the coefficients c_m. Thus multiplying the representation matrix $\mathbf{D}$ into the column vector $\mathbf{c}$ yields the column vector $\mathbf{c}'$ of the new coefficients after the transformation.

As a simple example, consider the p functions arising from $j = 1$. The basis functions are

$$\begin{aligned}
\varphi_1 &= -\sqrt{\frac{3}{8\pi}} \sin\theta\, e^{i\varphi} = -\sqrt{\frac{3}{8\pi}} \frac{x + iy}{r} \\
\varphi_0 &= \sqrt{\frac{3}{4\pi}} \cos\theta = \sqrt{\frac{3}{4\pi}} \frac{z}{r} \\
\varphi_{-1} &= \sqrt{\frac{3}{8\pi}} \sin\theta\, e^{-i\varphi} = \sqrt{\frac{3}{8\pi}} \frac{x - iy}{r}
\end{aligned} \tag{5-38}$$

We can form directed orbitals along the three axes by taking the three combinations

$$
\begin{aligned}
\psi_x &= \frac{1}{\sqrt{2}}(\varphi_{-1} - \varphi_1) \\
\psi_y &= \frac{i}{\sqrt{2}}(\varphi_{-1} + \varphi_1) \qquad (5\text{-}39) \\
\psi_z &= \varphi_0
\end{aligned}
$$

As we noted earlier, these three p functions transform under rotations like the three components of an ordinary vector. As an illustration, now consider the change in these functions produced by a rotation through the Eulerian angles $\alpha = 0$, $\beta = \pi/2$, $\gamma = \pi/4$. Then, from (5-36),

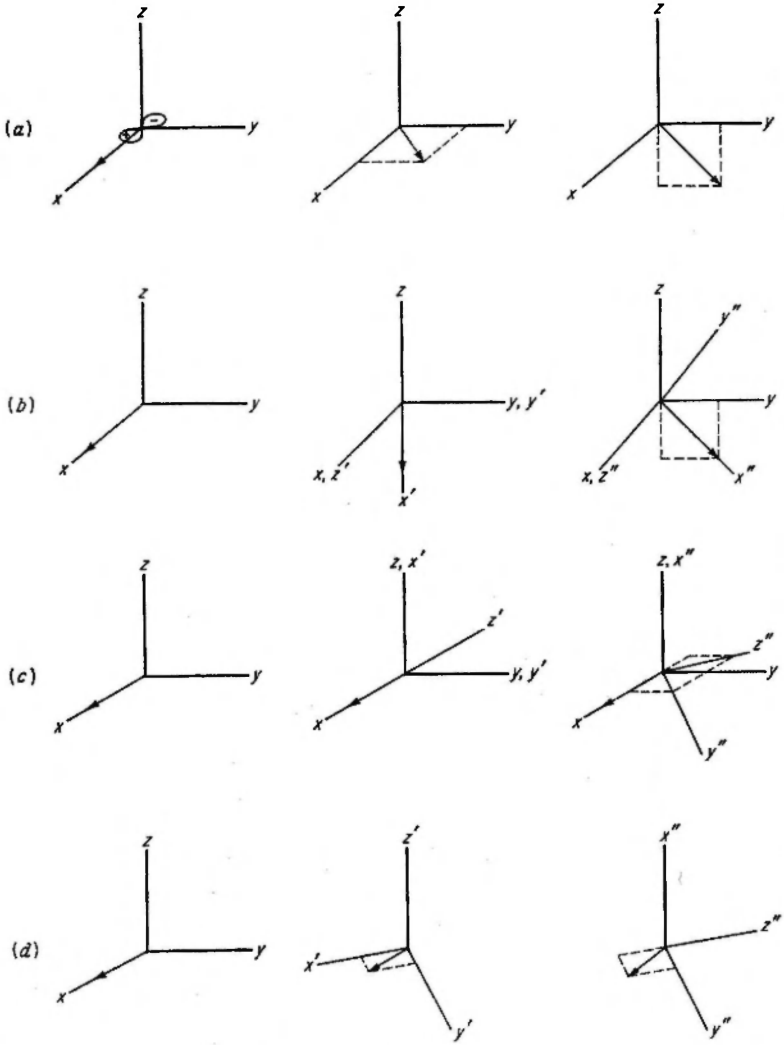
$$
\mathbf{D}^{(1)}\left(0, \frac{\pi}{2}, \frac{\pi}{4}\right) = \begin{bmatrix} \dfrac{1-i}{2\sqrt{2}} & -\dfrac{1}{\sqrt{2}} & \dfrac{1+i}{2\sqrt{2}} \\ \dfrac{1-i}{2} & 0 & -\dfrac{(1+i)}{2} \\ \dfrac{1-i}{2\sqrt{2}} & \dfrac{1}{\sqrt{2}} & \dfrac{1+i}{2\sqrt{2}} \end{bmatrix}
$$

Multiplying this into the column vectors representing ψ_x, ψ_y, and ψ_z, we find

$$
P\psi_x = \mathbf{D}^{(1)} \begin{pmatrix} -\dfrac{1}{\sqrt{2}} \\ 0 \\ \dfrac{1}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} \dfrac{i}{2} \\ -\dfrac{1}{\sqrt{2}} \\ \dfrac{i}{2} \end{pmatrix} = \frac{1}{\sqrt{2}}(\psi_y - \psi_z)
$$

$$
P\psi_y = \mathbf{D}^{(1)} \begin{pmatrix} \dfrac{i}{\sqrt{2}} \\ 0 \\ \dfrac{i}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} \dfrac{i}{2} \\ \dfrac{1}{\sqrt{2}} \\ \dfrac{i}{2} \end{pmatrix} = \frac{1}{\sqrt{2}}(\psi_y + \psi_z)
$$

$$
P\psi_z = \mathbf{D}^{(1)} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = \begin{pmatrix} -\dfrac{1}{\sqrt{2}} \\ 0 \\ \dfrac{1}{\sqrt{2}} \end{pmatrix} = \psi_x
$$


(a)
z
y
x
z
y
x
z
y
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(b)
z
y
x
z
y, y'
x, z'
x'
z
y''
y
x, z''
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(c)
z
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z, x''
z''
y
x
y''
(d)
z
y
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z'
x'
y'
x''
z''
y''

Fig. 5-4. *Successive rotations applied to ψ_x (a p function oriented along the x axi for Euler angles $\alpha = 0$, $\beta = \pi/2$, $\gamma = \pi/4$, as discussed in text. As illustrated in t first diagram, the arrow represents the direction of the positive lobe of the wav function. Cases (a) to (d) correspond to the four rows of Table 5-1. All four vie points lead to $(\psi_y - \psi_z)/\sqrt{2}$, as found in the text, but (a) and (d) are simplest to fol and are the most commonly used interpretations.*

Since these three directed p functions can be represented by unit vectors along the axes, it is easy to follow through the rotations and verify by geometrical inspection that the results found here correctly describe the effect of the rotations taken in any of the four interpretations listed in Table 5-1. The successive rotations are illustrated in Fig. 5-4. This inspection procedure would not be possible for higher j values, however, and so one must rely on the $\mathbf{D}^{(j)}$ matrices.

5-8 Vector Model for Addition of Angular Momenta

In this section we give the group-theoretical basis for the familiar vector-model rule of elementary atomic physics. This rule states that, when two angular momenta j_1 and j_2 are coupled together vectorially, the magnitude J of the resultant angular momentum $\mathbf{J}$ may have any of the integrally spaced values between $|j_1 - j_2|$ and $j_1 + j_2$.

Consider two systems of angular momentum j_1 and j_2. Each could be a single electron on the same atom provided that we take care of the Pauli principle by a separate consideration. In a central field, they will have $(2j_1 + 1)$- and $(2j_2 + 1)$-fold degeneracies, there being that many basis functions in the irreducible representations of the full rotation group. If we now combine the systems mentally, there will be $(2j_1 + 1) \times (2j_2 + 1)$ basis functions of the sort $u_{m_1}(1)v_{m_2}(2)$, and these will form a basis for a reducible representation of the rotation group which is the direct product of the two irreducible representations. With interactions between the systems allowed for, the various irreducible representations obtained by decomposing the direct-product representation can have different energies. We now seek the general rule governing this decomposition.

If we make a rotation R,

$$P_R u_{m_1}(1) = \sum_{m_1'} u_{m_1'}(1) D^{(j_1)}(R)_{m_1'm_1}$$

$$P_R v_{m_1}(2) = \sum_{m_2'} v_{m_2'}(2) D^{(j_2)}(R)_{m'_2m_2}$$

and hence

$$\begin{aligned} P_R u_{m_1}(1)v_{m_2}(2) &= \sum_{m_1',m_2'} u_{m_1'}(1)v_{m_2'}(2) D^{(j_1)}(R)_{m_1'm_1} D^{(j_2)}(R)_{m_2'm_2} \\ &= \sum_{m_1',m_2'} u_{m_1'}(1)v_{m_2'}(2)\Delta(R)_{m_1'm_2',m_1m_2} \end{aligned}$$

where $\mathbf{\Delta}(R)$ is the direct product

$$\mathbf{\Delta}(R) = \mathbf{D}^{(j_1)}(R) \times \mathbf{D}^{(j_2)}(R)$$

To decompose $\mathbf{\Delta}(R)$, we use the character rule

$$\chi^{(\Delta)}(R) = \chi^{(j_1)}(R)\chi^{(j_2)}(R) = \sum_J a_{j_1j_2J}\chi^{(J)}(R)$$

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Our formula (3-20) for $a_{j_1j_2J}$ is not very useful because there are an infinit number of classes. However, we can easily carry out the decompositio by inspection. Contracting $a_{j_1j_2J}$ to a_J, we require that

$$\chi(\alpha)^{(j_1)}\chi(\alpha)^{(j_2)} = \sum_{m_1=-j_1}^{j_1} e^{-im_1\alpha} \sum_{m_2=-j_2}^{j_2} e^{-im_2\alpha} = \sum_{m_1m_2} e^{-i(m_1+m_2)\alpha}$$
$$= \sum_{J=0}^{\infty} a_J \sum_{M=-J}^{J} e^{-iM\alpha}$$

Clearly $|M| \leq j_1 + j_2$. Thus the a_J vanish for $J > j_1 + j_2$. There is on term for $|M| = j_1 + j_2$; so $a_{j_1+j_2} = 1$. There will be two terms wit $M = j_1 + j_2 - 1$, namely, $(j_1 - 1) + j_2$ and $j_1 + (j_2 - 1)$. One of these i already accounted for by the sum with $a_{j_1+j_2}$, leaving one for the $(j_1 + j_2 - 1)$ sum. Continuing in this way, we find that all nonzero a_J are unity, so that we can write

$$\chi^{(j_1)}(\alpha)\chi^{(j_2)}(\alpha) = \sum_{J=|j_1-j_2|}^{j_1+j_2} \sum_{M=-J}^{J} e^{-iM\alpha} = \sum_{J=|j_1-j_2|}^{j_1+j_2} \chi^{(J)}(\alpha)$$

Hence it follows that

$$D^{(j_1)} \times D^{(j_2)} = \sum_{J=|j_1-j_2|}^{j_1+j_2} D^{(J)} = D^{(j_1+j_2)} + D^{(j_1+j_2-1)} + \cdots + D^{(|j_1-j_2|)} \tag{5-40}$$

That is, when two systems with angular momenta j_1 and j_2 are combined, the resulting state may have any of the angular momenta allowed by th elementary vector model.

Since the basis functions of each $D^{(J)}$ transform among themselves unde a rotation of the total system, they will still be degenerate even in the case o interaction between the two systems provided that the Hamiltonian i invariant under such overall rotations. For example, if we consider only the orbital angular momenta, we may combine two electrons in an atom with angular momenta l_1 and l_2 to get $L = |l_1 - l_2|, \ldots, l_1 + l_2$. Now th Hamiltonian is not invariant under a rotation of the coordinates of one electron, since the Coulomb repulsion depends on the relative position of the tw electrons. However, it *is* invariant under a joint rotation of both electrons. Hence $\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2$ is conserved, and L and M_L are good quantum number for representation labels. It should be noted, however, that one must no try to apply this result if, for example, one is combining angular moment of two systems with centers at separate points in space if the interactio depends on the direction of the axis between them. In this case, the Hamil tonian is clearly not invariant under even a joint rotation of coordinates unless of course one rotates the axis also. But then the total angula momentum would have to include that of the framework separating the tw centers as well as that of the two subsystems. To be specific, an *isotropic exchange coupling* $H' \sim \mathbf{j}_1 \cdot \mathbf{j}_2$ between two spins will leave $\mathbf{J} = \mathbf{j}_1 + \mathbf{j}_2$ as good quantum number, but *anisotropic exchange* or a simple dipole-dipole coupling will not, because in these cases there is another term

$$\sim(\mathbf{r}_{12}\cdot\mathbf{j}_1)(\mathbf{r}_{12}\cdot\mathbf{j}_2)$$

which depends on the direction of the separation vector $\mathbf{r}_{12}$.

5-9 The Wigner or Clebsch-Gordan Coefficients

The foregoing vector-model proof has shown that

$$D^{(j_1)} \times D^{(j_2)} = \sum_{J=|j_1-j_2|}^{j_1+j_2} D^{(J)}$$

This means that a similarity transformation must exist which reduces $\mathbf{D}^{(j_1)} \times \mathbf{D}^{(j_2)}$ to the block form

$$\mathbf{M}(R) = \begin{bmatrix} \mathbf{D}^{|j_1-j_2|}(R) & 0 & \cdots & 0 \\ 0 & \mathbf{D}^{|j_1-j_2|+1}(R) & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & \mathbf{D}^{(j_1+j_2)}(R) \end{bmatrix}$$

Expressed more compactly,

$$\mathbf{D}^{(j_1)}(R) \times \mathbf{D}^{(j_2)}(R) = \mathbf{A}^{-1}\mathbf{M}(R)\mathbf{A} \qquad M(R)_{J'M',JM} = \delta_{J'J}D^{(J)}{}_{M'M} \tag{5-41a}$$

where $\mathbf{A}$ is as yet an undetermined unitary matrix. This matrix $\mathbf{A}$ must be "square in the broader sense." That is, $\mathbf{A}$ has an equal number of rows and columns—$(2j_1 + 1)(2j_2 + 1) = \sum_J (2J + 1)$—but the rows are labeled by JM, whereas the columns are labeled by m_1m_2. A typical element from the matrix equation above is

$$D^{(j_1)}(R)_{m_1'm_1}D^{(j_2)}(R)_{m_2'm_2} = \sum_{J,M,M'} A^{-1}_{m_1'm_2',JM'}D^{(J)}(R)_{M'M}A_{JM,m_1m_2} \tag{5-41b}$$

The matrix $\mathbf{A}$ is useful because it prescribes the linear combinations of the $u_{m_1}v_{m_2}$ functions which are to be taken so as to diagonalize the total angular momentum J and its z component M, namely,

$$\psi_M{}^J = \sum_{m_1m_2} u_{m_1}v_{m_2}(A^{-1})_{m_1m_2,JM} \tag{5-42a}$$

and conversely

$$u_{m_1}v_{m_2} = \sum_{JM} \psi_M{}^J A_{JM,m_1m_2} \tag{5-42b}$$

Of course, since $\mathbf{A}$ is unitary, $\mathbf{A}^{-1} = \mathbf{A}^\dagger = \mathbf{A}^*$. In fact, we shall find a matrix $\mathbf{A}$ which is real. Therefore $\mathbf{A}^{-1} = \mathbf{A}$.

First, we confirm that if $\mathbf{A}$ satisfies (5-41) then these linear combinations do in fact transform according to $\mathbf{D}^{(J)}$, this being the only real requirement for the identification of $\psi_M{}^J$. We consider a rotation R to be applied to (5-42*a*),

$$\begin{aligned}
P_R\psi_M{}^J &- \sum_{m_1m_2} P_R u_{m_1} P_R v_{m_2} (A^{-1})_{m_1m_2,JM} \\
&= \sum_{m_1m_2,m_1'm_2'} u_{m_1'} v_{m_2'} D^{(j_1)}(R)_{m_1'm_1} D^{(j_2)}(R)_{m_2'm_2} (A^{-1})_{m_1m_2,JM} \\
&= \sum_{m_1m_2,m_1'm_2',J'M'} \psi_{M'}{}^{J'} A_{J'M',m_1'm_2'} D^{(j_1)}(R)_{m_1'm_1} \\
&\quad \times D^{(j_2)}(R)_{m_2'm_2} (A^{-1})_{m_1m_2,JM} \\
&= \sum_{J'M'} \psi_{M'}{}^{J'} [\mathbf{A}(\mathbf{D}^{(j_1)} \times \mathbf{D}^{(j_2)})\mathbf{A}^{-1}]_{J'M',JM} \\
&= \sum_{J'M'} \psi_{M'}{}^{J'} [\mathbf{M(R)}]_{J'M',JM} \\
&= \sum_{J'M'} \psi_{M'}{}^{J'} D^{(J)}(R)_{M'M}\, \delta_{J'J} \\
&= \sum_{M'} \psi_{M'}{}^{J} D^{(J)}(R)_{M'M}
\end{aligned}$$

Thus we have verified that the matrices $\mathbf{A}^{-1}$ give the linear combinations of $u_{m_1}v_{m_2}$ which transform properly under a joint rotation of the axes of both the systems being combined. If such a rotation leaves the Hamiltonian invariant even in the presence of interaction, these $\psi_M{}^J$ are the "proper linear combinations" for the combined system. This suggests the utility of the matrix of coefficients in practical problems where we are combining such angular momenta as $\mathbf{L} + \mathbf{S} = \mathbf{J}$ (the classic example), $\mathbf{j}_1 + \mathbf{j}_2 = \mathbf{J}$ (*j-j* coupling), $\mathbf{I} + \mathbf{J} = \mathbf{F}$ (hyperfine coupling), and even isotopic spin in nuclear theory. This last application may seem a bit surprising at first, since isotopic spin is not an angular momentum at all. However, since our group-theoretical development was based only on rotational invariance, it is clearly not restricted to rotations in ordinary space. It works equally well in isotopic-spin space.

Determination of coefficients. The Wigner coefficients which we seek are simply the elements of the matrix $\mathbf{A}$ with the properties which we have just sketched. Let us now proceed to determine this matrix explicitly. We start by considering the effect of a rotation by α about the z axis. We can express this in two different ways,

$$P_R\psi_M{}^J = e^{-iM\alpha}\psi_M{}^J = e^{-iM\alpha} \sum_{m_1,m_2} u_{m_1}v_{m_2}A^{-1}_{m_1m_2,JM}$$

or

$$P_R \sum_{m_1,m_2} u_{m_1}v_{m_2}A^{-1}_{m_1m_2,JM} = \sum_{m_1,m_2} e^{-im_1\alpha}u_{m_1}e^{-im_2\alpha}v_{m_2}A^{-1}_{m_1m_2,JM}$$

Since the $u_{m_1}v_{m_2}$ form an orthonormal set, the coefficient of each term in the sum must be the same as the corresponding one in the other (equivalent) sum. This will be true only if the only nonvanishing $A_{m_1m_2,JM}$ occur when

$$M = m_1 + m_2$$

This restriction expresses the conservation of J_z, though it was obtained from a consideration of transformation properties. We can now condense our notation slightly, by setting

$$A_{JM,m_1m_2} = a_{Jm_1m_2}\delta_{M,m_1+m_2}$$

In terms of **a**, we may express (5-41*b*) as

$$D^{(j_1)}(R)_{m_1'm_1}D^{(j_2)}(R)_{m_2'm_2} = \sum_{J=|j_1-j_2|}^{j_1+j_2} a^{-1}_{m_1'm_2'J}D^{(J)}(R)_{m_1'+m_2',\,m_1+m_2}a_{Jm_1m_2} \quad (5\text{-}43)$$

Note that the multiple summation has been reduced to only a single sum over J.

The next step is to note that **A** is fixed by our conditions only within multiplication by a diagonal matrix of the form $V_{J'M'.JM} = w_J\delta_{J'J}\delta_{M'M}$, where $|w_J| = 1$. We see this by noting that a **V** of this form commutes with $\mathbf{M}(R)$ and hence that $(\mathbf{VA})^{-1}\mathbf{M}(\mathbf{VA}) = \mathbf{A}^{-1}\mathbf{V}^{-1}\mathbf{MVA} = \mathbf{A}^{-1}\mathbf{MV}^{-1}\mathbf{VA} = \mathbf{A}^{-1}\mathbf{MA}$. This degree of freedom allows us an arbitrary phase choice for each value of J in **A**. We use this freedom to choose $A_{J,j_1-j_2;j_1,-j_2} = a_{J,j_1,-j_2} = |a_{J,j_1,-j_2}|$ so that these elements are real and positive.

Now we proceed by multiplying through (5-43) by $D^{(J')}(R)^*_{m_1'+m_2',m_1+m_2}$, integrating over R, and using the orthogonality theorem. By using the unitarity of **A**, this can be written

$$\int D^{(j_1)}(R)_{m_1'm_1}D^{(j_2)}(R)_{m_2'm_2}D^{(J')}(R)^*_{m_1'+m_2',m_1+m_2}\,dR$$
$$= \sum_J a^*_{Jm_1'm_2'}a_{Jm_1m_2}\int D^{(J)}(R)_{m_1'+m_2',m_1+m_2}D^{(J')}(R)^*_{m_1'+m_2',m_1+m_2}\,dR \quad (5\text{-}44)$$

By orthogonality, the right member vanishes unless $J = J'$. This reduces the sum to a single term, and we now change notation by dropping the prime on J. The right member is then $a^*_{Jm_1'm_2'}a_{Jm_1m_2}[\int dR/(2J+1)]$.

Now make the special choice $m_1' = j_1$, $m_2' = -j_2$. Then our phase convention assures us that $a_{Jm_1'm_2'}$ is real and positive. Further, in these special cases, our general formula (5-35) for $\mathbf{D}^{(j)}(R)$ reduces to a single term, as illustrated for $\mathbf{U}^{(j)}(\mathbf{u})$ in (5-31). Upon taking advantage of this simplification, but using the general formula for $D^{(J)}(R)^*$, the left member of (5-44) becomes

$$\binom{2j_1}{j_1-m_1}^{\frac{1}{2}}\binom{2j_2}{j_2-m_2}^{\frac{1}{2}}$$
$$\times\sum_\kappa \frac{(-1)^{\kappa+j_2+m_2}[(J+m_1+m_2)!\,(J-m_1-m_2)!\times(J+j_1-j_2)!\,(J-j_1+j_2)!]^{\frac{1}{2}}}{(J-j_1+j_2-\kappa)!\,(J+m_1+m_2-\kappa)!\,\kappa!\,(\kappa+j_1-j_2-m_1-m_2)!}$$
$$\times\int\left(\cos\frac{\beta}{2}\right)^{2(J+j_2+m_1-\kappa)}\left(\sin\frac{\beta}{2}\right)^{2(j_1-m_1+\kappa)}dR \quad (5\text{-}45)$$

[The notation $\binom{n}{m}$ signifies the binomial coefficient $n!/m!\,(n-m)!$.] Thi integral may be related to the normalization integral $\int dR$ by converting it to the form of a normalization integral for the simple special case $(m' = j)$,

$$\int |D^{(j)}(R)_{jm}|^2\,dR = \binom{2j}{j-m} \int \left(\cos\frac{\beta}{2}\right)^{2(j+m)} \left(\sin\frac{\beta}{2}\right)^{2(j-m)} dR = \frac{\int dR}{2j+1}$$

To make the connection, set

$$j + m = J + j_2 + m_1 - \kappa \qquad \qquad j = \frac{J + j_1 + j_2}{2}$$

$$\text{or}$$

$$j - m = j_1 - m_1 + \kappa \qquad \qquad m = \frac{J + j_2 - j_1 + 2m_1 - 2\kappa}{2}$$

Then the integral in (5-45) is just

$$\frac{\int dR}{J + j_1 + j_2 + 1} \frac{1}{\binom{2j}{j-m}} = \frac{\int dR}{J + j_1 + j_2 + 1} \frac{(J + j_2 + m_1 - \kappa)!\,(j_1 - m_1 + \kappa)!}{(J + j_1 + j_2)!}$$

$$= \frac{(J + j_2 + m_1 - \kappa)!\,(j_1 - m_1 + \kappa)!}{(J + j_1 + j_2 + 1)!} \int dR$$

Inserting this in (5-45) and then (5-45) into (5-44), canceling the $\int dR$, an multiplying through by $(2J + 1)$ leads to

$$\begin{aligned} &a^*_{J,j_1,-j_2} a_{Jm_1m_2} \\ &= (2J+1) \sum_\kappa \frac{(-1)^{\kappa+j_2+m_2} [(2j_1)!\,(2j_2)!\,(J + m_1 + m_2)!\,(J - m_1 - m_2)! \times (J + j_1 - j_2)!\,(J - j_1 + j_2)!]}{(J + j_1 + j_2 + 1)!\,[(j_1 - m_1)!\,(j_1 + m_1)!\,(j_2 - m_2)!\,(j_2 + m_2)!]} \\ &\quad \times \frac{(J + j_2 + m_1 - \kappa)!\,(j_1 - m_1 + \kappa)!}{(J - j_1 + j_2 - \kappa)!\,(J + m_1 + m_2 - \kappa)!\,\kappa!\,(\kappa + j_1 - j_2 - m_1 - m_2)!} \end{aligned} \qquad (5\text{-}4$$

Now we can immediately determine $a_{J,j_1,-j_2}$ by setting $m_1 = j_1$ and m_2 $-j_2$ and then taking the positive square root of the right member of (5-46 After an algebraic reduction given by Wigner,[1] we obtain

$$a_{J,j_1,-j_2} = \left[\frac{(2J + 1)(2j_1)!\,(2j_2)!}{(J + j_1 + j_2 + 1)!\,(j_1 + j_2 - J)!}\right]^{\frac{1}{2}}$$

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[1] E. Wigner, "Group Theory," p. 194, Academic Press, Inc., New York, 1959.

Factoring this out of (5-46) and introducing a more complete notation to indicate all the angular momenta involved, we have our final result,

$$A^{j_1j_2J}_{m_1m_2M} = a^{(j_1j_2)}_{Jm_1m_2} \frac{[(J+j_1-j_2)!\,(J-j_1+j_2)!\,(j_1+j_2-J)!\,(J+m_1+m_2)!\,(J-m_1-m_2)!]^{\frac{1}{2}}}{[(J+j_1+j_2+1)!\,(j_1-m_1)!\,(j_1+m_1)!\,(j_2-m_2)!\,(j_2+m_2)!]^{\frac{1}{2}}}$$
$$\times \sum_{\kappa}{}' \frac{(-1)^{\kappa+j_2+m_2}\sqrt{(2J+1)}(J+j_2+m_1-\kappa)!\,(j_1-m_1+\kappa)!}{(J-j_1+j_2-\kappa)!\,(J+m_1+m_2-\kappa)!\,\kappa!\,(\kappa+j_1-j_2-m_1-m_2)!} \tag{5-47}$$

In this equation the summation extends over all values of κ for which the factorials in the denominator do not become infinite. (Recall that $0! = 1$, but factorials of negative integers are infinite.) Note that all the coefficients are real, so that $\mathbf{A}^{-1} = \tilde{\mathbf{A}}$. Though hard to see from this form, the coefficient is unchanged (except for a possible sign change) when we interchange (j_1, m_1) with (j_2, m_2) in the formula. Such symmetry is clearly necessary if the formula is to be correct.

In the case $m_1 + m_2 = M = J$, only the term with $\kappa = J - j_1 + j_2$ survives in (5-47), and we obtain the relatively simple result

$$a_{J,m_1,J-m_1} = (-1)^{j_1-m_1}$$
$$\times \frac{[(2J+1)!\,(j_1+j_2-J)!\,(j_1+m_1)!\,(J+j_2-m_1)!]^{\frac{1}{2}}}{[(J+j_1+j_2+1)!\,(J+j_1-j_2)!\,(J-j_1+j_2)!\,(j_1-m_1)!\,(j_2-J+m_1)!]^{\frac{1}{2}}} \tag{5-48}$$

We note that this is positive whenever $m_1 = j_1$, as chosen in our convention. In particular, consider the "stretched case," where $J = j_1 + j_2$ and $M = J$. Then $m_1 = j_1$, $m_2 = j_2$, and (5-48) reduces to unity, as it must since this is the only way by which $M = j_1 + j_2$ can be obtained.

We have now finished deriving explicit formulas for the famous Wigner or Clebsch-Gordan coefficients. They are the coefficients for the combination of subsystem angular-momentum eigenfunctions to form eigenfunctions of the total angular momentum according to the formula

$$\psi_M{}^J = \sum_m a^{(j_1j_2)}_{J,m,M-m} u_m^{(j_1)} v_{M-m}^{(j_2)} = \sum_m A^{j_1j_2J}_{m,M-m,M} u_m^{(j_1)} v_{M-m}^{(j_2)} \tag{5-49}$$

Since $M = m_1 + m_2$ in all cases, we shall often abbreviate the latter notation from $A^{j_1j_2J}_{m_1m_2M}$ to $A^{j_1j_2J}_{m_1m_2}$.

5-10 Notation, Tabulations, and Symmetry Properties of the Wigner Coefficients

The formula (5-47) is very cumbersome to use, though completely general and explicit. Alternative methods exist for finding the coefficients in specific cases by use of recursion formulas. These methods have been described by various authors, and many different systems of notation have been developed. In this section, we survey this literature to make it accessible for detailed use.

One of the most useful single tabulations is that of Condon and Shortley.[1] They tabulate explicit formulas for $j_2 = \frac{1}{2}$, 1, $\frac{3}{2}$, and 2 for general values of all the other parameters. [In their notation, $A^{j_1 j_2 j_3}_{m_1 m_2 m_3} = a^{(j_1 j_2)}_{j, m_1 m_2} = (j_1 j_2 m_1 m_2 \,|\, j_1 j_2 j_3 m_3)$]. These results handle all problems in which the smaller of the two angular momenta to be added does not exceed 2. A similar table for $j_2 = \frac{5}{2}$ has been given by Saito and Morita,[2] and one for $j_2 = 3$ has been given by Falkoff, Colladay, and Sells.[3] A decimal tabulation has been given by Simon[4] for cases in which all angular momenta are less than $\frac{9}{2}$. More convenient for many purposes are the *non*decimal tables giving the coefficients as square roots of rational fractions, due to Cohen. These are reproduced as an appendix in Heine's book[5] for all cases where $j_1 + j_2 \leqslant 4$.

The number of coefficients which need to be tabulated is reduced by many symmetry relations which govern the effect of permutation of indices and changes of sign. These results are also useful for extracting results of a general nature in the consideration of particular problems. These symmetry properties are extensively discussed in the books of Rose, of Edmonds, and of Rotenberg et al.[6] To facilitate the discussion of these symmetry properties, symmetrized vector-coupling coefficients have been introduced by many authors. These are based on the idea that, by reversing the sense of the resultant $\mathbf{j} = \mathbf{j}_3$, one has $\mathbf{j}_1 + \mathbf{j}_2 + \mathbf{j}_3 = 0$, in which all three j's enter equivalently. The first of these symmetrized forms seems to have been the V coefficients of Racah.[7] These are related to the Wigner or Clebsch-Gordan coefficients by the relation

$$V(j_1 j_2 j_3, m_1 m_2 m_3) = (-1)^{j_3 - m_3}(2j_3 + 1)^{-\frac{1}{2}} A^{j_1 j_2 j_3}_{m_1 m_2 -m_3} \tag{5-50}$$

More recently, Wigner introduced his so-called "3-j symbol,"[8] which is related to the V coefficients by a simple phase change, namely,

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_3 + j_2 - j_1} V(j_1 j_2 j_3, m_1 m_2 m_3) \tag{5-51}$$

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[1] Condon and Shortley, *op. cit.*, pp. 76–77.

[2] R. Saito and M. Morita, *Progr. Theoret. Phys.* (*Kyoto*), **13**, 540 (1955).

[3] D. L. Falkoff, G. S. Colladay, and R. E. Sells, *Can. J. Phys.*, **30**, 253 (1952).

[4] A. Simon, *Oak Ridge Natl. Lab. Rept.* ORNL-1718 (1954).

[5] V. Heine, "Group Theory," Pergamon Press, New York, 1960.

[6] M. E. Rose, *op. cit.*, chap. 3; A. R. Edmonds, "Angular Momentum in Quantum Mechanics," chap. 3, Princeton University Press, Princeton, N.J., 1957; M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, Jr., "The 3-j and 6-j Symbols," Technology Press, Cambridge, Mass., 1959.

[7] G. Racah, *Phys. Rev.*, **62**, 438 (1942).

[8] See, for example, Wigner, *op. cit.*, chap. 24.

This 3-j symbol is equal to Schwinger's[1] X coefficient $X(j_1j_2j_3, m_1m_2m_3)$. The advantage of these symmetrized coefficients is that the introduction of the statistical weight factor $(2j_3 + 1)^{-\frac{1}{2}}$ removes an asymmetry between j_3 and j_1, j_2. The symmetry properties of the 3-j symbols (or the X coefficients) are as follows:

Equality under cyclic permutation of columns

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_3 & j_1 \\ m_2 & m_3 & m_1 \end{pmatrix} = \begin{pmatrix} j_3 & j_1 & j_2 \\ m_3 & m_1 & m_2 \end{pmatrix} \tag{5-52a}$$

Possible sign change under interchange of two columns

$$\begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} = \begin{pmatrix} j_1 & j_3 & j_2 \\ m_1 & m_3 & m_2 \end{pmatrix} = \begin{pmatrix} j_3 & j_2 & j_1 \\ m_3 & m_2 & m_1 \end{pmatrix}$$

$$= (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \tag{5-52b}$$

Possible sign change on replacement of m by $-m$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \tag{5-52c}$$

From the relations (5-50) and (5-51) analogous results can be obtained from (5-52) for the somewhat less symmetrical V coefficients and for the ordinary unsymmetrized Wigner or Clebsch-Gordan coefficients. An exhaustive numerical tabulation of these 3-j symbols, covering all cases for $j_1, j_2, j_3 \leqslant 8$, has been given by Rotenberg et al. in the book cited above.

Table 5-2

Wigner coefficients for $j_2 = \frac{1}{2}$

$j_2 = \frac{1}{2}$	$m_2 = \frac{1}{2}$	$m_2 = -\frac{1}{2}$
$j = j_1 + \frac{1}{2}$	$\left(\dfrac{j_1 + m + \frac{1}{2}}{2j_1 + 1}\right)^{\frac{1}{2}}$	$\left(\dfrac{j_1 - m + \frac{1}{2}}{2j_1 + 1}\right)^{\frac{1}{2}}$
$j = j_1 - \frac{1}{2}$	$-\left(\dfrac{j_1 - m + \frac{1}{2}}{2j_1 + 1}\right)^{\frac{1}{2}}$	$\left(\dfrac{j_1 + m + \frac{1}{2}}{2j_1 + 1}\right)^{\frac{1}{2}}$

We conclude this section by quoting the explicit form of the Wigner coefficients (in the ordinary unsymmetrized form) for some simple cases. The case of $j = \frac{1}{2}$ is particularly important because it gives the formulas for combining the spin angular momentum of an electron with its orbital angular momentum. The coefficients for this case are given in Table 5-2.

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[1] J. Schwinger, On Angular Momentum, *USAEC Rept.* NYO-3071 (1952).

For example, then,

$$\psi_m^{(l+\frac{1}{2})} = \left(\frac{l+m+\frac{1}{2}}{2l+1}\right)^{\frac{1}{2}} u_{m-\frac{1}{2}}^{(l)} v_{\frac{1}{2}}^{(\frac{1}{2})} + \left(\frac{l-m+\frac{1}{2}}{2l+1}\right)^{\frac{1}{2}} u_{m+\frac{1}{2}}^{(l)} v_{-\frac{1}{2}}^{(\frac{1}{2})}$$

Specializing further, if $l - 1$, we have the states

$$\psi_{\frac{3}{2}}^{(\frac{3}{2})} = u_1^{(1)} v_{\frac{1}{2}}^{(\frac{1}{2})}$$

$$\psi_{\frac{1}{2}}^{(\frac{3}{2})} = \sqrt{\tfrac{2}{3}}\, u_0^{(1)} v_{\frac{1}{2}}^{(\frac{1}{2})} + \sqrt{\tfrac{1}{3}}\, u_1^{(1)} v_{-\frac{1}{2}}^{(\frac{1}{2})}$$

and similar expressions for $\psi_{-\frac{1}{2}}^{(\frac{3}{2})}$ and $\psi_{-\frac{3}{2}}^{(\frac{3}{2})}$.

Table 5-3

The Wigner coefficients for $j_2 - 1$

$j_2 - 1$	$m_2 = 1$	$m_2 = 0$	$m_2 = -1$
$j = j_1 + 1$	$\left[\frac{(j_1+m)(j_1+m+1)}{(2j_1+1)(2j_1+2)}\right]^{\frac{1}{2}}$	$\left[\frac{(j_1-m+1)(j_1+m+1)}{(2j_1+1)(j_1+1)}\right]^{\frac{1}{2}}$	$\left[\frac{(j_1-m)(j_1-m+1}{(2j_1+1)(2j_1+2)}\right.$
$j = j_1$	$-\left[\frac{(j_1+m)(j_1-m+1)}{2j_1(j_1+1)}\right]^{\frac{1}{2}}$	$\frac{m}{[j_1(j_1+1)]^{\frac{1}{2}}}$	$\left[\frac{(j_1-m)(j_1+m+1}{2j_1(j_1+1)}\right.$
$j = j_1 - 1$	$\left[\frac{(j_1-m)(j_1-m+1)}{2j_1(2j_1+1)}\right]^{\frac{1}{2}}$	$-\left[\frac{(j_1-m)(j_1+m)}{j_1(2j_1+1)}\right]^{\frac{1}{2}}$	$\left[\frac{(j_1+m+1)(j_1+}{2j_1(2j_1+1)}\right.$

The coefficients for the case $j_2 = 1$ are given in Table 5-3. We shall find these coefficients very useful in the next sections in conjunction with the Wigner-Eckart theorem when applied to vector operators.

5-11 Tensor Operators

Scalar operators. A scalar S is defined as a quantity which is invariant under all rotations. Hence, we can apply the general theorem (Sec. 4-9) on matrix elements of invariant operators to conclude that there will be no matrix elements of a scalar operator connecting functions belonging to different irreducible representations (or different rows of the same one) of the full rotation group. For example, there are no matrix elements of the energy between states with different J or M in an atom, because the Hamiltonian is invariant under rotation and hence is a scalar. Moreover, all states within one irreducible representation have the same diagonal matrix elements (of energy, in our example). Expressed symbolically,

$$S_{N'j'm',Njm} = (\psi_{N'j'm'}, S\psi_{Njm}) = (N'j'm' \,|S|\, Njm)$$

$$= \delta_{jj'}\delta_{mm'}(N'j \,\|S\|\, Nj) \tag{5-53}$$

where we have used N to indicate all other quantum numbers which are irrelevant to the discussion of rotational properties. The quantity $(N'j\|S\|Nj)$ is a *reduced matrix element* which may depend on N, N', and j but is independent of m.

We now proceed to work out generalizations of this theorem for operators with more complicated rotational properties.

Vector operators. To obtain a general definition of the transformed operator O' related to the operator O by a coordinate transformation $\mathbf{R}$, we require that

$$O'\psi' = (O\psi)'$$

where $\psi' = P_R\psi$ is the transformed wavefunction. Applying this, we have

$$O'P_R\psi = P_RO\psi$$

But the relation must hold for arbitrary ψ. Hence, we have the operator equality

$$O'P_R = P_RO$$

or

$$O' = P_ROP_R^{-1} \tag{5-54}$$

An operator $\mathbf{V}$ is said to be a vector operator if it has three components (V_x, V_y, V_z) which transform like (x, y, z) under a coordinate transformation $\mathbf{R}$. That is,

$$\mathbf{V}' = P_R\mathbf{V}P_R^{-1} = \mathbf{R}^{-1}\mathbf{V} \tag{5-55}$$

where $\mathbf{R}^{-1}$ enters because of our convention that $P_Rf(\mathbf{x}) = f(\mathbf{R}^{-1}\mathbf{x})$. Expressing a component of this equation in cartesian form, we have

$$V_i' = P_RV_iP_R^{-1} = \sum_j (R^{-1})_{ij}V_j = \sum_j V_jR_{ji} \tag{5-56}$$

since for a real orthogonal transformation $\mathbf{R}^{-1} = \tilde{\mathbf{R}}$.

To illustrate these rather formal rules, consider the example $\mathbf{V} = \boldsymbol{\nabla}$, and let $\mathbf{R}$ represent a rotation by $\pi/2$ about z. Then

$$\mathbf{R} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

and accordingly $P_Rf(x, y, z) = f(-y, x, z)$ and $P_R^{-1}f(x, y, z) = f(y, -x, z)$. Hence

$$P_RV_xP_R^{-1}\psi(x, y, z) = P_R\frac{\partial}{\partial x}\psi(y, -x, z) = \frac{\partial}{\partial(-y)}\psi(x, y, z) = -V_y\psi(x, y, z)$$

which is just what is required by the definition of a vector operator.

Although these cartesian coordinates are satisfactory here, it is often more convenient to introduce *spherical components* based on the rotational eigenfunctions. These will be much easier to generalize further. Conforming to our standard phase conventions, we define

$$
\begin{aligned}
V_1 &= -\frac{V_x + iV_y}{\sqrt{2}} = \frac{-V_+}{\sqrt{2}} \\
V_0 &= V_z \\
V_{-1} &= \frac{V_x - iV_y}{\sqrt{2}} = \frac{V_-}{\sqrt{2}}
\end{aligned}
\tag{5-57}
$$

One must be careful in expressing a vector in terms of these components because

$$
\mathbf{V} = V_x\mathbf{u}_x + V_y\mathbf{u}_y + V_z\mathbf{u}_z = -V_{-1}\mathbf{u}_1 + V_0\mathbf{u}_0 - V_1\mathbf{u}_{-1} = \sum_{\mu=-1}^{1} (-1)^\mu V_{-\mu}\mathbf{u}_\mu \tag{5-58}
$$

where the **u**'s are unit vectors and $\mathbf{u}_{\pm 1} = \mp(\mathbf{u}_x \pm i\mathbf{u}_y)/\sqrt{2}$, $\mathbf{u}_0 = \mathbf{u}_z$. The orthonormality relation of these new unit vectors is $\mathbf{u}_\mu \cdot \mathbf{u}_{\mu'} = \delta_{\mu,-\mu'}(-1)^\mu$, as is easily verified from their definition. Therefore the ordinary scalar product of two vectors has the form

$$
\begin{aligned}
\mathbf{V} \cdot \mathbf{W} &= \sum_{\mu\mu'} (-1)^{\mu+\mu'} V_{-\mu} W_{-\mu'} \mathbf{u}_\mu \cdot \mathbf{u}_{\mu'} \\
&= \sum_{\mu} (-1)^\mu V_{-\mu} W_\mu
\end{aligned}
\tag{5-59}
$$

If **V** has real cartesian components, this is equivalent to $\sum_\mu V_\mu^* W_\mu$, our definition of the Hermitian scalar product.

Since these new spherical components have been set up to have the same structure as the angular-momentum eigenfunctions for $j = 1$, they must have the same transformation properties, namely,

$$
P_R V_\mu P_R^{-1} = \sum_{\mu'} V_{\mu'} D^{(1)}(R)_{\mu'\mu} \tag{5-60}
$$

Tensor operators. The spherical vectors of the previous section are readily generalized to *spherical tensors* or *irreducible tensors* of arbitrary rank. We define an irreducible-tensor operator of the ωth rank to be an operator with $(2\omega + 1)$ components $T_\mu^{(\omega)}$ which transform under rotations according to

$$
P_R T_\mu^{(\omega)} P_R^{-1} = \sum_{\mu'} T_{\mu'}^{(\omega)} D^{(\omega)}(R)_{\mu'\mu} \tag{5-61}
$$

These irreducible tensors have considerable advantages over ordinary cartesian tensors. For example, a cartesian tensor of rank 2 has $3^2 = 9$ components $T_{ij}(i, j = x, y, z)$. The component T_{xy} is a quantity with the same transformation properties as the product of the coordinates xy. If a rotation of coordinates is carried out, these T_{ij} are transformed into new components T'_{ij} which are linear combinations of the old according to

$$T'_{ij} = \sum_{kl} T_{kl} R_{ki} R_{lj} \tag{5-62}$$

where R_{ki} is the matrix of direction cosines specifying the corresponding coordinate transformation. Hence, if we treat the double subscript ij as a single index α, the $T_{ij} = T_\alpha$ form a basis for a nine-dimensional representation of the rotation group, $T'_\alpha = \sum_\beta T_\beta \Gamma(R)_{\beta\alpha}$ with $\Gamma(R)_{\beta\alpha} = \Gamma(R)_{kl,ij} = R_{ki}R_{lj}$, or $\mathbf{\Gamma}(R) = \mathbf{R} \times \mathbf{R}$. Since we have already seen that the coordinates (x, y, z) transform according to $D^{(1)}$ (within a unitary transformation), evidently $R \times R = D^{(1)} \times D^{(1)} = D^{(0)} + D^{(1)} + D^{(2)}$ by the vector-model principle. Thus, under the group of rotations, the representation based on the nine components of a second-rank cartesian tensor may be decomposed into simpler one, three, and five-dimensional representations having the transformation properties of $D^{(0)}$, $D^{(1)}$, and $D^{(2)}$. These are examples of the irreducible tensors introduced at the beginning of this section. In general, a cartesian tensor of rank r may be decomposed into irreducible tensors whose ranks may be determined by successive applications of the vector-model principle. For example, a third-rank tensor T_{ijk} has 27 components. It may be decomposed as follows,

$$\begin{aligned} D^{(1)} \times D^{(1)} \times D^{(1)} &= D^{(1)} \times [D^{(0)} + D^{(1)} + D^{(2)}] \\ &= D^{(1)} + [D^{(0)} + D^{(1)} + D^{(2)}] + [D^{(1)} + D^{(2)} + D^{(3)}] \\ &= D^{(0)} + 3D^{(1)} + 2D^{(2)} + D^{(3)} \end{aligned}$$

into seven distinct irreducible tensors of ranks 0 through 3. Evidently there will always be just one irreducible tensor of rank equal to that of the cartesian tensor being reduced.

Let us return to the decomposition of the cartesian second-rank tensor to see the nature of the irreducible tensors in more detail. First, let us note that the trace of a tensor

$$T = \operatorname{Tr} \mathbf{T} = \sum_i T_{ii}$$

is a scalar, or a quantity invariant under any unitary transformation such as a rotation of axes. Hence it forms a basis for $D^{(0)}$. Next, consider the three antisymmetric combinations obtained from

$$A_z = \tfrac{1}{2}(T_{xy} - T_{yx})$$

by cyclic permutation. Note that this A_z will transform under rotation like $(V_x U_y - V_y U_x)$, where $\mathbf{V}$ and $\mathbf{U}$ are arbitrary vectors. But this expression is just the z component of the vector product $\mathbf{V} \times \mathbf{U}$, which transforms as a vector under rotation (but as an axial vector under inversion since **V** and **U** are polar vectors). Hence the elements A_x, A_y, and A_z form a basis for a three-dimensional irreducible representation equivalent to $D^{(1)}$. Note that if the tensor **T** were antisymmetric (or "skew-symmetric"), it would be completely specified by these three elements, and would have the form

$$\begin{pmatrix} 0 & A_z & -A_y \\ -A_z & 0 & A_x \\ A_y & -A_x & 0 \end{pmatrix}$$

Since the elements of such an antisymmetric tensor transform under rotations like those of a vector but go into themselves under inversion of coordinates, such a tensor is the prototype form of an axial vector.

Finally, we find the basis of the five-dimensional irreducible representation by forming the traceless symmetric tensor **S** with elements

$$S_{ij} = \tfrac{1}{2}(T_{ij} + T_{ji}) - \tfrac{1}{3}T$$

This has six elements, but only two of the diagonal ones are independent since the trace is zero. Thus one could choose five elements which contain all the information, and these would serve as the basis of a five-dimensional *irreducible* representation. A convenient choice of five elements in terms of cartesian coordinates is the set suggested by the five *d* functions we used earlier in discussing crystal-field splittings, namely, S_{xy}, S_{yz}, S_{zx}, $S_{xx} - S_{yy}$, $2S_{zz} - S_{xx} - S_{yy}$. However, to use the $\mathbf{D}^{(2)}$ matrices to represent the transformation properties, we must use the five functions with the same symmetry as the angular-momentum eigenfunctions $\varphi_m{}^{(2)}$. These differ from the abovementioned set (after normalization) by only a unitary transformation.

As a specific example, consider the electric field gradient tensor, whose elements are

$$\varphi_{ij} = \frac{\partial^2\varphi}{\partial x_i\,\partial x_j} = \frac{-\partial E_i}{\partial x_j} = \frac{-\partial E_j}{\partial x_i}$$

The invariant is $\sum_i \varphi_{ii} = \nabla^2\varphi = -4\pi\rho$, which certainly is independent of orientation of the axes. The antisymmetric tensor vanishes because, e.g.,

$$A_z = \frac{1}{2}\left[\frac{\partial^2\varphi}{\partial x\,\partial y} - \frac{\partial^2\varphi}{\partial y\,\partial x}\right] = 0$$

The remaining five elements could be taken to be φ_{xy}, φ_{yz}, φ_{zx}, $\varphi_{xx} - \varphi_{yy}$, $2\varphi_{zz} - \varphi_{xx} - \varphi_{yy}$. These elements give all the information required to calculate the quadrupole coupling, for example.

It having been seen how the cartesian tensors are built up by considering the transformation properties of products of cartesian coordinates, it is not surprising that we can take the same approach for the spherical tensors.

That is, if we have two vectors with spherical components $V_{\pm 1,0}$ and $U_{\pm 1,0}$, then we can consider the nine cross products as forming a basis for a reducible representation of the rotation group. By the same argument given above, this decomposes into $D^{(0)}$, $D^{(1)}$, and $D^{(2)}$. We get the invariant from the scalar product

$$T_0^{\,0} = \sum_{\mu} (-1)^{\mu} V_{\mu} U_{-\mu} \tag{5-63a}$$

the vector from such antisymmetric products as

$$T_{\pm 1}^{(1)} \sim (V_{\pm 1} U_0 - V_0 U_{\pm 1}) \qquad T_0^{(1)} \sim (V_1 U_{-1} - V_{-1} U_1) \tag{5-63b}$$

and the second-rank tensor from the symmetric combinations, i.e.,

$$\begin{gathered} T_{\pm 2}^{(2)} \sim V_{\pm 1} U_{\pm 1} \qquad T_{\pm 1}^{(2)} \sim (V_{\pm 1} U_0 + V_0 U_{\pm 1}) \\ T_0^{(2)} \sim [2 V_0 U_0 + (V_1 U_{-1} + V_{-1} U_1)] \end{gathered} \tag{5-63c}$$

These linear combinations are specified by the Wigner coefficients for combining $j_1 = 1$ and $j_2 = 1$ to form $J = 0$, 1, and 2, respectively. This technique can be extended indefinitely to work out possible structures for the higher-rank spherical tensors.

Two spherical tensors may be multiplied and contracted according to the rule

$$T_M^{\ (\Omega)}(A_1, A_2) = \sum_{\mu_1} a^{(\omega_1 \omega_2)}_{\Omega, \mu_1, M-\mu_1} T_{\mu_1}^{\ (\omega_1)}(A_1) T^{(\omega_2)}_{M-\mu_1}(A_2) \tag{5-64}$$

where a is the appropriate Wigner coefficient. This formula is exactly analogous to the one for combining angular-momentum eigenfunctions, and it may be proved in exactly the same way by using only the transformation properties of the T_{μ} under rotations. From this formula we see that, when tensors are multiplied, we combine the ranks according to the vector model. A particularly important example is the formation of a tensor of zero rank (a scalar invariant) by the combination of two tensors of the same rank. In this case the Wigner coefficient is just $(-1)^{\omega_1 - \mu_1}(2\omega_1 + 1)^{-\frac{1}{2}}$. Dropping the factors which are independent of μ in $T_0^{(0)}$, we have the invariant

$$\mathscr{I}(A_1, A_2) = \sum_{\mu} (-1)^{\mu} T_{\mu}^{\ (\omega)}(A_1) T_{-\mu}^{\ (\omega)}(A_2) \tag{5-65}$$

This invariant is often called the *scalar product of the two tensors*. We note that it reduces to the definition of the scalar product for three-dimensional vectors as found previously. Such forms play a prominent role in the expression of any rotationally invariant Hamiltonian which depends on two types of variables.

An example of considerable importance is interaction of two dipoles. The classical expression

$$H = \frac{\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2}{r_{12}^{\ 3}} - \frac{3(\boldsymbol{\mu}_1 \cdot \mathbf{r}_{12})(\boldsymbol{\mu}_2 \cdot \mathbf{r}_{12})}{r_{12}^{\ 5}} \tag{5-65a}$$

can be expanded into the following form (with $\boldsymbol{\mu} = \gamma\hbar\mathbf{I}$),

$$H = \gamma^2\hbar^2 r_{12}^{-3}(A + B + C + D + E + F)$$

where

$$A = I_z^{(1)} I_z^{(2)}(3\cos^2\theta_{12} - 1)$$

$$B = -\tfrac{1}{4}(I_-^{(1)} I_+^{(2)} + I_+^{(1)} I_-^{(2)})(3\cos^2\theta_{12} - 1)$$

$$C = \tfrac{3}{2}(I_+^{(1)} I_z^{(2)} + I_z^{(1)} I_+^{(2)}) \sin\theta_{12}\cos\theta_{12} e^{-i\varphi_{12}} \tag{5-65b}$$

$$D = \tfrac{3}{2}(I_-^{(1)} I_z^{(2)} + I_z^{(1)} I_-^{(2)}) \sin\theta_{12}\cos\theta_{12} e^{i\varphi_{12}}$$

$$E = \tfrac{3}{4} I_+^{(1)} I_+^{(2)} \sin^2\theta_{12} e^{-2i\varphi_{12}}$$

$$F = \tfrac{3}{4} I_-^{(1)} I_-^{(2)} \sin^2\theta_{12} e^{2i\varphi_{12}}$$

In these expressions θ_{12} and φ_{12} are the angles specifying the orientation of the vector $\mathbf{r}_{12}$. The terms A and B both belong to $\mu = 0$, as is clear from the angular dependence ($3\cos^2\theta_{12} - 1$). If the spin parts of A and B are summed together, they equal

$$\tfrac{1}{2}[2I_z^{(1)} I_z^{(2)} - I_x^{(1)} I_x^{(2)} - I_y^{(1)} I_y^{(2)}] = \tfrac{1}{2}[2I_0^{(1)} I_0^{(2)} + I_1^{(1)} I_{-1}^{(2)} + I_-^{(1)} I_1^{(2)}]$$

in terms of cartesian or spherical components. In either form the expression is easily recognized to have the characteristic transformation property of $T_0^{(2)}$. C and D belong to $\mu = \pm 1$, and E and F belong to $\mu = \pm 2$. In all cases the factor involving the spins $\mathbf{I}^{(1)}$ and $\mathbf{I}^{(2)}$ is of the form given in (5-63c). On the other hand, the factor involving θ_{12} and φ_{12} is simply a spherical harmonic of order 2. Decomposition of H in this manner gives a clear physical picture of the interaction in terms of spin flips produced by a time variation of the spatial coordinates θ_{12} and φ_{12}.

Another example having the same structure could be set up representing the interaction of a nuclear quadrupole-moment tensor with the electric field gradient tensor which we discussed earlier in the section. This example is deferred to a later chapter, however.

We conclude this section by pointing out that Racah defines these same irreducible operators by their commutation relations with angular-momentum operators.

$$[J_\pm, T_\mu^{(\omega)}] = [\omega(\omega + 1) - \mu(\mu \pm 1)]^{\frac{1}{2}} T_{\mu\pm 1}^{(\omega)} \tag{5-66a}$$

and

$$[J_z, T_\mu^{(\omega)}] = \mu T_\mu^{(\omega)} \tag{5-66b}$$

The angular-momentum operators themselves satisfy these rules for $\omega = 1$. Since we have shown that the rotational transformation properties of angular-momentum operators are equivalent to the commutation relations, it is not surprising that Racah's definition of a general spherical tensor operator is equivalent to our definition through transformation properties. This equivalence may be verified by consideration of infinitesimal rotations.

5-12 The Wigner-Eckart Theorem

This very useful theorem provides the generalization of the matrix-element theorem for scalar operators to the higher tensor operators. We consider a general matrix element, apply a unitary transformation P_R (which does not change the value of the matrix element), and obtain

$$
\begin{aligned}
&(N'j'm'\,|T_\mu{}^{(\omega)}|\,Njm)\\
&\qquad = (P_R\psi_{N'j'm'}, P_R T_\mu{}^{(\omega)} P_R{}^{-1} P_R\psi_{Njm})\\
&\qquad = \Big(\sum_{m''}\psi_{N'j'm''}D^{(j')}(R)_{m''m'}, \sum_{\mu'} T_{\mu'}{}^{(\omega)} D^{(\omega)}(R)_{\mu'\mu}\sum_{m'''}\psi_{Njm'''}D^{(j)}(R)_{m'''m}\Big)\\
&\qquad = \sum_{\mu'm''m'''} D^{(j')}(R)^*_{m''m'} D^{(\omega)}(R)_{\mu'\mu} D^{(j)}(R)_{m'''m} (N'j'm''\,|T_{\mu'}{}^{(\omega)}|\,Njm''')
\end{aligned}
$$

Now, in the case of the scalar operator, $\mathbf{D}^{(\omega)} = \mathbf{D}^{(0)} = 1$, and we could integrate over R and apply the orthogonality theorem for representations to obtain the result. To handle the general case of a product of three representations, we just combine the last two by use of the Wigner coefficients using (5-41).

$$
D^{(\omega)}(R)_{\mu'\mu} D^{(j)}(R)_{m'''m} = \sum_{J=|j-\omega|}^{j+\omega} A^{j\omega J}_{m'''\mu'} D^{(J)}(R)_{m'''+\mu', m+\mu} A^{j\omega J}_{m\mu}
$$

In this we have used the fact that $\mathbf{A}$ is real. Inserting this expression above, we have

$$
\begin{aligned}
(N'j'm'\,|T_\mu{}^{(\omega)}|\,Njm) = \sum_{J\mu'm''m'''} & A^{j\omega J}_{m'''\mu'} A^{j\omega J}_{m\mu} D^{(j')}(R)^*_{m''m'} D^{(J)}(R)_{m'''+\mu', m+\mu}\\
& \times (N'j'm''\,|T_{\mu'}{}^{(\omega)}|\,Njm''')
\end{aligned}
$$

If we integrate over R and divide by the volume of group-element space $\int dR$, the orthonormality of the $\mathbf{D}$'s leads to

$$
\begin{aligned}
(N'j'm'\,|T_\mu{}^{(\omega)}|\,Njm) = \sum_{J=|j-\omega|}^{j+\omega} \sum_{\mu'm''m'''} & A^{j\omega J}_{m'''\mu'} A^{j\omega J}_{m\mu} \frac{\delta_{Jj'}\delta_{m'''+\mu', m''}\delta_{m+\mu, m'}}{2j'+1}\\
& \times (N'j'm''\,|T_{\mu'}{}^{(\omega)}|\,Njm''')
\end{aligned}
$$

Note that the matrix element vanishes unless $|j-\omega| < j' < j+\omega$. Even if this inequality is satisfied, there is only one term in the sum on J, namely, $J = j'$. We may rewrite this nonvanishing term as

$$
\begin{aligned}
&(N'j'm'\,|T_\mu{}^{(\omega)}|\,Njm)\\
&\qquad = A^{j\omega j'}_{m\mu}\delta_{m', m+\mu} \sum_{\mu'm''m'''} \frac{A^{j\omega j'}_{m'''\mu'}\delta_{m'''+\mu', m''}(N'j'm''\,|T_{\mu'}{}^{(\omega)}|\,Njm''')}{2j'+1}
\end{aligned}
$$

We see that the sum is independent of m, m', μ and depends only on N, N', j, j'. Thus we may denote it by $(N'j' \| T^{(\omega)} \| Nj)$ and then obtain our theorem

$$(N'j'm' \,|T_{\mu}^{(\omega)}|\, Njm) = A^{j\omega j'}_{m\mu} \delta_{m',m+\mu} (N'j' \| T^{(\omega)} \| Nj)$$
$$|j - \omega| \leqslant j' \leqslant (j + \omega) \qquad \blacktriangleright \text{(5-67)}$$

The quantity $(N'j' \| T^{(\omega)} \| Nj)$ is called the *reduced matrix element* of $T^{(\omega)}$.

This result reduces the amount of calculation required to handle a problem, since the tabulated Wigner coefficients give the ratios of matrix elements of all components of a tensor operator between all states of given initial and final angular momentum. Thus one need calculate only one such matrix element to determine the reduced matrix element. This is usually done for the simple choice $\mu = 0$, $m = m'$. It should accordingly be emphasized that the *form* of the result (5-67) is all that is essential from this development. The reduced matrix element is almost invariably determined by using (5-67) together with one explicitly calculated matrix element. The summation expression for the reduced matrix element given above from the derivation is of no use for calculation.

This theorem also gives us two very general *selection rules* on matrix elements,

$$\begin{aligned} |\Delta j| &= |j - j'| \leqslant \omega \\ \Delta m &= m' - m = \mu \leqslant \omega \end{aligned} \qquad \blacktriangleright \text{(5-68)}$$

For example, for dipole transitions, T is a vector operator, and so $\omega = 1$. Therefore $\Delta j = \pm 1$, 0. For circularly polarized radiation about the z axis, $\mu = \pm 1 = \Delta m$. For radiation polarized along the quantization axis, $\mu = 0 = \Delta m$.

Matrix elements of vector operators. The most important single example of the use of the Wigner-Eckart theorem (5-67) is the determination of the matrix elements of a vector operator. (These results are also obtained by Condon and Shortley[1] by using the commutation rules.) Suppressing the N, N' notation (although it is still implicit) and using the tabulated Wigner coefficients (although absorbing some normalization constants into the reduced matrix elements), we have the following nonvanishing elements:

$$\begin{aligned}
(J+1, M \pm 1 \,|V_{\pm}|\, JM) &= \mp (J+1 \| V \| J)[(J \pm M + 1)(J \pm M + 2)]^{\frac{1}{2}} \\
(J+1, M \,|V_z|\, JM) &= (J+1 \| V \| J)[(J + M + 1)(J - M + 1)]^{\frac{1}{2}} \\
(J, M \pm 1 \,|V_{\pm}|\, JM) &= (J \| V \| J)[(J \mp M)(J \pm M + 1)]^{\frac{1}{2}} \\
&= (J \| V \| J)(J, M \pm 1 \,|J_{\pm}|\, JM) \qquad \blacktriangleright \text{(5-69)} \\
(JM \,|V_z|\, JM) &= (J \| V \| J)M = (J \| V \| J)(JM \,|J_z|\, JM) \\
(J-1, M \pm 1 \,|\, V_{\pm}|\, JM) &= \pm (J-1 \| V \| J)[(J \mp M)(J \mp M - 1)]^{\frac{1}{2}} \\
(J-1, M \,|V_z|\, JM) &= (J-1 \| V \| J)[(J + M)(J - M)]^{\frac{1}{2}}
\end{aligned}$$

---

[1] Condon and Shortley, *op. cit.*, p. 63.

Note that we give the elements for $V_\pm = V_x \pm iV_y = \mp\sqrt{2}V_{\pm 1}$ since these are more commonly used than the spherical components $V_{\pm 1}$ themselves. Also note that, by absorbing some common factors from the Wigner coefficients into the reduced matrix elements, we have changed the normalization of the reduced matrix elements in (5-69) compared with those in (5-67). By using these results we can calculate, for example, the relative intensities of various Zeeman components $M \to M'$ of a given transition $J \to J'$ for any polarization. We also note in general that, if $J = J' = 0$, all matrix elements of V vanish. Thus we have our final selection rule, namely, $J = 0 \to 0$ *transitions are forbidden.* [This result could have been anticipated from the vector-model result that, when one combines $\omega = 1$ (for the dipole transition) with $J = 0$, one obtains *only* $J = 1$ for the final state.] Finally, we note that the matrix elements diagonal in J are proportional to the corresponding matrix elements of $\mathbf{J}$ itself. We shall make much use of this fact in later chapters by using $\mathbf{J}$ as an operator replacement for other *vector* operators. Apart from the proportionality constant $(J\|V\|J)$, we see that this is a rigorous replacement for matrix elements diagonal in J. For our applications, this fact is the most important single result of this section.

5-13 The Racah Coefficients

The Wigner or Clebsch-Gordan coefficients which we have discussed provide the unitary transformation for coupling two angular momenta j_1, j_2 together to form a resultant j. It often occurs that one must couple *three* angular momenta together. This can be done by successive use of the Wigner coefficients, but it is worth working out a number of general properties once and for all. The Racah coefficients relate the various coupling schemes which may be used in coupling $\mathbf{j}_1 + \mathbf{j}_2 + \mathbf{j}_3 = \mathbf{j}$. In this section and the following one, we shall survey these coefficients and their application.

Given $\mathbf{j}_1$, $\mathbf{j}_2$, and $\mathbf{j}_3$, we can have six simultaneously diagonalized operators, for example, $\mathbf{j}_1^2$, $\mathbf{j}_2^2$, $\mathbf{j}_3^2$, j_{1z}, j_{2z}, j_{3z}. However, we are more interested in representations which diagonalize $\mathbf{j}^2$ and j_z as well as the magnitudes j_1, j_2, j_3. In this case the sixth diagonal operator is $\mathbf{j}^2_{\text{int}}$, the square of an intermediate angular momentum formed by compounding two of the three. This $\mathbf{j}_{\text{int}}$ can be chosen in three ways. We consider the two,

$$\mathbf{j}_{\text{int}} = \mathbf{j}' = \mathbf{j}_1 + \mathbf{j}_2 \qquad \mathbf{j}_{\text{int}} = \mathbf{j}'' = \mathbf{j}_2 + \mathbf{j}_3$$

The relation between either of these and the third possibility could be obtained by a suitable renumbering. Now a unitary transformation $\mathbf{R}$ must exist between the eigenfunctions of the basis which diagonalizes j' and that which diagonalizes j''. Suppressing the quantum numbers j_1, j_2, j_3, which carry throughout, we write this relation as

$$\psi_m{}^j(j') = \sum_{j''} \psi_m{}^j(j'') R_{j''j'} \tag{5-70}$$

The Racah coefficients W are then defined by the following relation:

$$R_{j''j'} = [(2j''+1)(2j'+1)]^{\frac{1}{2}} W(j_1 j_2 j j_3,\, j'j'') \tag{5-71}$$

The square root is introduced here, just as with Racah's V coefficients, to enhance the symmetry properties.

We now use the Wigner coefficients to work out some properties of the W coefficients. As before, we denote the Wigner coefficient for combining $\mathbf{j}_1 + \mathbf{j}_2 = \mathbf{j}$ by $A^{j_1 j_2 j}_{m_1 m_2}$. It is, of course, understood that $m = m_1 + m_2$. Then

$$\psi_{m'}{}^{j'} = \sum_{m_1} A^{j_1 j_2 j'}_{m_1, m'-m_1} \psi_{m_1}{}^{j_1} \psi_{m'-m_1}^{j_2}$$

Using these, we can build up

$$\psi_m{}^j(j') = \sum_{m'} A^{j' j_3 j}_{m', m-m'} \psi^{j_3}_{m-m'} \sum_{m_1} A^{j_1 j_2 j'}_{m_1, m'-m_1} \psi_{m_1}{}^{j_1} \psi^{j_2}_{m'-m_1}$$

In a similar manner

$$\psi_m{}^j(j'') = \sum_{m''} A^{j_1 j'' j}_{m-m'', m''} \psi^{j_1}_{m-m''} \sum_{m_2} A^{j_2 j_3 j''}_{m_2, m''-m_2} \psi_{m_2}{}^{j_2} \psi^{j_3}_{m''-m_2}$$

Inserting these in (5-70) and equating coefficients of $\psi_{\mu_1}{}^{j_1}\psi_{\mu_2}{}^{j_2}\psi_{\mu_3}{}^{j_3}$ on both sides (noting that $\mu_1 + \mu_2 + \mu_3 = m$), we obtain

$$A^{j_1 j_2 j'}_{\mu_1 \mu_2} A^{j' j_3 j}_{\mu_1+\mu_2, \mu_3} = \sum_{j''} R_{j''j'} A^{j_2 j_3 j''}_{\mu_2 \mu_3} A^{j_1 j'' j}_{\mu_1, \mu_2+\mu_3} \tag{5-72}$$

We can now transform this into more useful forms by taking advantage of the unitary nature of the A's. For example, if we multiply by $A^{j_2 j_3 j''}_{\mu_2 \mu_3}$ for some particular j'' and sum over μ_2, holding $\mu_2 + \mu_3$ fixed, we obtain

$$\sum_{\mu_2} A^{j_1 j_2 j'}_{\mu_1 \mu_2} A^{j' j_3 j}_{\mu_1+\mu_2, \mu_3} A^{j_2 j_3 j''}_{\mu_2 \mu_3} = R_{j''j'} A^{j_1 j'' j}_{\mu_1, \mu_2+\mu_3} \tag{5-73}$$

If we now multiply through by $A^{j_1 j'' j}_{\mu_1, \mu_2+\mu_3}$ and sum on μ_1, holding

$$\mu_1 + \mu_2 + \mu_3 = \text{constant},$$

we obtain

$$\sum_{\mu_1} \sum_{\mu_2} A^{j_1 j_2 j'}_{\mu_1 \mu_2} A^{j' j_3 j}_{\mu_1+\mu_2, \mu_3} A^{j_2 j_3 j''}_{\mu_2 \mu_3} A^{j_1 j'' j}_{\mu_1, \mu_2+\mu_3} = R_{j''j'} \tag{5-74}$$

Combining (5-74) with (5-71) provides an explicit definition of the Racah coefficients in terms of the Wigner coefficients which we have determined previously. We note that the Racah coefficients are independent of all magnetic quantum numbers. We see that they cannot depend on m by inspection of (5-70), since application of J_+ or J_- to (5-70) changes the value of m while multiplying both sides by the same factor. Hence $R_{j''j'}$ must be independent of m.

In discussing the properties of the W coefficients it is customary to lighten the notation by replacing $(j_1 j_2 j j_3; j' j'')$ by $(abcd; ef)$ and also replacing $m_1 m_2 m m_3$ by $\alpha\beta\gamma\delta$, so that $\gamma = \alpha + \beta + \delta$. In this notation, the relations (5-74) and (5-71) lead to

$$W(abcd; ef) = [(2e+1)(2f+1)]^{-\frac{1}{2}} \sum_{\alpha,\beta} A^{abe}_{\alpha\beta} A^{edc}_{\alpha+\beta,\delta} A^{bdf}_{\beta\delta} A^{afc}_{\alpha,\beta+\delta} \tag{5-75}$$

which explicitly defines the Racah coefficients. Racah was able to carry out the indicated summation and obtain the following expression:

$$\begin{aligned} W(abcd; ef) = {} & \Delta(abe)\Delta(cde)\Delta(acf)\Delta(bdf) \\ & \cdot \sum_\kappa \frac{(-1)^{\kappa+a+b+c+d}(\kappa+1)!}{\begin{aligned}(\kappa-a-b-e)!\,(\kappa-c-d-e)! \\ \times (\kappa-a-c-f)!\,(\kappa-b-d-f)!\,(a+b+c+d-\kappa)! \\ \times (a+d+e+f-\kappa)!\,(b+c+e+f-\kappa)!\end{aligned}} \end{aligned} \tag{5-76}$$

In this, the "triangle coefficients" are defined by

$$\Delta(abc) = \left[\frac{(a+b-c)!\,(a-b+c)!\,(-a+b+c)!}{(a+b+c+1)!}\right]^{\frac{1}{2}}$$

This expression is finite only if a, b, c satisfy the "triangular condition" that $\mathbf{a} + \mathbf{b} = \mathbf{c}$ be allowed by the vector model. That is, the difference of any two must not exceed the third. Thus we expect the selection rule that $W(abcd; ef)$ cannot occur unless (abe), (edc), (bdf), and (afc) satisfy the triangular condition. In fact detailed consideration shows that there will be an infinite denominator (the factorial of a negative integer) for all terms in the sum in (5-76) if the triangular conditions are not satisfied. Thus these coefficients have a value of zero. This is reasonable, since otherwise we would have nonphysical coupling arrangements. The situation can be visualized graphically by a vector-model quadrilateral in which the two intermediate angular momenta form the diagonals. Such a quadrilateral is shown in Fig. 5-5.

Properties of the Racah coefficients. The roles of the six angular momenta in $W(abcd; ef)$ may be interchanged in 24 ways while the triangular relations are still preserved. The only effect of such permutations is a possible phase change. Detailed consideration shows that the following permutations leave the coefficient unchanged:

$$(abcd; ef)(badc; ef)(cdab; ef)(dcba; ef)(acbd; fe)(cadb; fe)(bdac; fe)(dbca; fe) \tag{5-77a}$$

The following permutations give $(-1)^{b+c-e-f}W(abcd; ef)$:

$$(aefd; bc)(eadf; bc)(fdae; bc)(dfea; bc)(afed; cb)(fade; cb)(edaf; cb)(defa; c \qquad (5\text{-}77$$

The following give $(-1)^{a+d-e-f}W(abcd; ef)$:

$$(ebcf; ad)(befc; ad)(cfeb; ad)(fcbe; ad)(ecbf; da)(cefb; da)(bfec; da)(fbce; d \qquad (5\text{-}77$$

By use of these relations, any index can be moved to any position for th purpose of carrying out calculations.

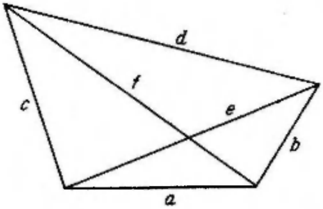

Fig. 5-5. *Vector-model quadrilateral showi the relation of the six coupled angular momen involved in a Racah coefficient.*

Whenever the area of one of the triangles vanishes, i.e., when one membe of a triad in (5-76) equals the sum of the other two, the sum reduces to single term. For example, if $e = a + b$, then both $(\kappa - a - b - c - d)$ and $(a + b + c + d - \kappa)!$ appear in the denominator. The only value o κ which keeps these both finite is $\kappa = a + b + c + d$, in which case both are $0! = 1$. In this way we obtain

$$W(abcd; a + b, f)$$

$$= \left[\frac{(2a)!\,(2b)!\,(a + b + c - d)!\,(a + b + c + d + 1)!\,(a + b + d - c)!}{(2a + 2b + 1)!\,(a + c + f + 1)!\,(c + d - a - b)!\,(b + f + d + 1)!} \times \frac{(c + f - a)!\,(d + f - b)!}{(a + c - f)!\,(a + f - c)!\,(b + d - f)!\,(b + f - d)!}\right]^{\frac{1}{2}} \qquad (5\text{-}78)$$

By use of the symmetry relations of the preceding paragraph, (5-78) may be used in general when any of the four triangles has vanishing area.

Another simple special case occurs when one of the arguments of W vanishes. This causes the quadrilateral to reduce to a triangle. A simple reduction using the symmetry properties leads to

$$W(abcd; 0f) = \frac{(-1)^{f-b-d}\delta_{ab}\delta_{cd}}{[(2b + 1)(2d + 1)]^{\frac{1}{2}}} \qquad (5\text{-}79)$$

Since the $R_{j''j'} = R_{fe}$ form a unitary transformation, we have the orthonormality relations

$$\sum_e R_{fe}R_{ge} = \delta_{fg}$$

By using the definition (5-71), this implies the following orthonormality property of the Racah coefficients:

$$\sum_e (2e + 1)(2f + 1)W(abcd; ef)W(abcd; eg) = \delta_{fg} \tag{5-80}$$

Another useful sum over W coefficients is Racah's sum rule,

$$\sum_e (2e + 1)(-1)^{a+b-e}W(abcd; ef)W(bacd; eg) = W(agfb; cd) \tag{5-81}$$

Obviously these coefficients are even more awkward to handle algebraically than the Wigner coefficients. Considerable effort has been expended in preparing helpful tables. A useful source of algebraic expressions for $e = \frac{1}{2}$, 1, $\frac{3}{2}$, and 2 is the review article of Biedenharn, Blatt, and Rose.[1] Extensive numerical tables, covering all cases for angular momenta up to 8 in steps of $\frac{1}{2}$, are given in the book of Rotenberg et al.[2] Actually, they tabulate the so-called 6-j coefficients, related to Racah's W coefficients by a phase factor, namely,

$$W(abcd; ef) = (-1)^{a+b+c+d}\begin{Bmatrix} a & b & e \\ d & c & f \end{Bmatrix}$$

so as to have improved symmetry characteristics.

5-14 Application of Racah Coefficients

The Racah coefficients have proved useful in an extremely wide range of applications. The unifying characteristic is the importance of states of definite angular momentum. Examples of these areas are atomic and molecular spectra, angular correlation of nuclear radiation, angular distributions in nuclear reactions, and multipole-field expansions.

An important type of application arises in evaluating matrix elements of a rotationally invariant operator, such as a term in a Hamiltonian, which is expressed as the contraction of two irreducible tensors of rank L. We may denote this as follows:

$$T^{(L)}(1) \cdot T^{(L)}(2) = \sum_M (-1)^M T_M{}^{(L)}(1)T_{-M}{}^{(L)}(2)$$

This represents an interaction between two independent subsystems 1 and 2, each characterized by its own angular momentum. For example, if this represented the spin-orbit coupling, system 1 is the orbital motion with angular momentum $j_1 = l$ and system 2 is the spin with $j_2 = s$. Regardless of the value of l, though, these two tensors are both of rank $L = 1$, since all angular momenta are (axial) vector operators.

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[1] L. C. Biedenharn, J. M. Blatt, and M. E. Rose, *Revs. Modern Phys.*, **24**, 249 (1952).

[2] Rotenberg, Bivins, Metropolis, and Wooten, *op. cit.*

In general we are interested in matrix elements of the type

$$(j_1'j_2'j'm'\;|T^{(L)}(1)\cdot T^{(L)}(2)|\;j_1j_2jm)$$

We can express the initial and final states in terms of decoupled states, using the Wigner coefficients,

$$\psi_m{}^j = \sum_{m_1} \psi_{m_1}{}^{j_1}\psi_{m-m_1}^{j_2}A^{j_1j_2j}_{m_1,m-m_1}$$

$$\psi_{m'}{}^{j'} = \sum_{m_1'} \psi_{m_1'}^{j_1'}\psi_{m'-m_1}^{j_2'}A^{j_1'j_2'j'}_{m_1',m'-m_1'}$$

By using these, the matrix element becomes

$$\sum_{Mm_1'm_1} (-1)^M A^{j_1'j_2'j'}_{m_1',m'-m_1'}A^{j_1j_2j}_{m_1,m-m_1}(j_1'm_1'\;|T_M{}^{(L)}(1)|\;j_1m_1)$$
$$\times\;(j_2',\,m'-m_1'\;|T_{-M}{}^{(L)}(2)|\;j_2,\,m-m_1)$$

if we take advantage of the chance of factoring the matrix element which arises because the two factors operate in separate decoupled spaces. We may now apply the Wigner-Eckart theorem to each of these factored matrix elements. For example,

$$(j_1'm_1'\;|T_M{}^{(L)}(1)|\;j_1m_1) = (j_1'\;\|T^{(L)}(1)\|\;j_1)A^{j_1Lj_1'}_{m_1M}\,\delta_{m_1',M+m_1}$$

We may also apply the Wigner-Eckart theorem to the entire matrix element $T^{(L)}(1)\cdot T^{(L)}(2)$. Since it is an invariant (tensor of zero rank), we have

$$\begin{aligned}(j'm'\;|T^{(L)}(1)\cdot T^{(L)}(2)|\;jm) &= A^{j0j'}_{m0}\delta_{m'm}(j\;\|T^{(L)}(1)\cdot T^{(L)}(2)\|\;j') \\ &= \delta_{j'j}\delta_{m'm}(j\;\|T^{(L)}(1)\cdot T^{(L)}(2)\|\;j)\end{aligned} \qquad (5\text{-}82)$$

Thus, as expected, the matrix element vanishes unless $j' = j$ and $m' = m$. Now, if we combine the pieces set up above, taking advantage of the fact that $M = m_1' - m_1$ to eliminate one summation, we have

$$(j_1j_2j'm'\;|T^{(L)}(1)\cdot T^{(L)}(2)|\;j_1j_2jm) = \delta_{m'm}\delta_{j'j}(j_1\;\|T^{(L)}(1)\|\;j_1)(j_2\;\|T^{(L)}(2)\|\;j_2)$$
$$\times \sum_{m_1m_1'} (-1)^{m_1'-m_1}A^{j_1j_2j}_{m_1,m-m_1}A^{j_2Lj_2'}_{m-m_1,m_1-m_1'}A^{j_1Lj_1'}_{m_1,m_1'-m_1}A^{j_1'j_2'j'}_{m_1',m'-m_1'}$$

By suitable juggling of indices and use of the symmetry properties of th Wigner coefficients, this sum can be brought into the form (5-75) definin the Racah coefficients. In this way we can express the matrix element i terms of a single Racah coefficient, which can be found in the tables. Th final result is

$$(j_1j_2j'm'\;|T^{(L)}(1)\cdot T^{(L)}(2)|\;j_1j_2jm) = \delta_{m'm}\delta_{j'j}(-1)^{j_1'+j_2-j}W(j_1j_2j_1'j_2';jL)$$
$$\times\;[(2j_1'+1)(2j_2'+1)]^{\frac{1}{2}}(j_1'\;\|T^{(L)}(1)\|\;j_1)(j_2'\;\|\;T^{(L)}(2)\|\;j_2) \qquad (5\text{-}8$$

In view of (5-82), we see that the Racah coefficient can be considered to express the reduced matrix element of the contraction $T^{(L)}(1) \cdot T^{(L)}(2)$ in terms of the reduced matrix elements of $T^{(L)}(1)$ in the j_1m_1 representation and of $T^{(L)}(2)$ in the j_2m_2 representation. Since these are relatively easy to calculate, this is a considerable simplification.

Another important result which may be obtained by similar manipulation[1] is an expression for the matrix elements of one of the tensors $T^{(L)}(1)$, which operates on only part of the system, in the coupled representation which diagonalizes the *total* angular momentum. This result is an example of the general Wigner-Eckart theorem;

$$(j_1'j_2j'm' \,|T_M^{(L)}(1)|\, j_1j_2jm) = A^{jLj'}_{mM}\delta_{m',m+M}(j_1'j_2'j' \,\|T^{(L)}(1)\|\, j_1j_2j) \quad (5\text{-}84a)$$

but in this case the Racah coefficients explicitly relate the reduced matrix element with that in the decoupled representation, which is relatively easy to calculate.

$$(j_1'j_2j' \,\|T^{(L)}(1)\|\, j_1j_2j) = \delta_{j_2'j_2}(-1)^{j_2+L-j_1-j}\,[(2j_1'+1)(2j+1)]^{\frac{1}{2}}$$
$$\times\, W(j_1jj_1'j';j_2L)(j_1' \,\|T^{(L)}(1)\|\, j_1) \quad (5\text{-}84b)$$

5-15 The Rotation-Inversion Group

We have now completed our study of the group of all proper rotations. This group represents a large part of the symmetry of many physical systems. However, as we noted in the previous chapter, in many cases we also have symmetry under inversion as well as under proper rotations. Operations containing the inversion as well as a rotation are referred to as *improper* rotations. They are quite distinct from the proper rotations and have the property of turning a right-handed into a left-handed coordinate system, for example. Clearly no proper rotation could accomplish this, since all proper rotations can be built up out of infinitesimal rotations. The combined group formed as the direct product of the group of the inversion with the pure rotation group is called the *rotation-inversion group*, the *rotation-reflection group*, the *full orthogonal group* (as opposed to the orthogonal group with determinant +1, which gives the pure rotations), or, in the German literature, the *Drehspiegelungsgruppe*.

The coordinate transformation matrix of the inversion operator i in x, y, z coordinate space is simply

$$\mathbf{i} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

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[1] See, for example, Rose's book, *op. cit.*, p. 118.

which changes **r** into −**r**. Obviously this matrix commutes with all the 3×3 rotation matrices. Thus we may form the direct-product group in the simple manner indicated in Sec. 3-9. As noted there, this leads to two irreducible representations of the direct-product group for each one of the proper-rotation group. The *positive*, or *even*, one of these is just the same for proper and improper rotations, whereas the *negative*, or *odd*, one has all signs changed for improper rotations. That is,

$$\begin{aligned} D_+^{(l)}(iR) &= D_+^{(l)}(R) \\ D_-^{(l)}(iR) &= -D_-^{(l)}(R) \end{aligned} \tag{5-85}$$

We have used l rather than j to label the representations here because these simple considerations are valid only for the single-valued representations arising from integral angular momenta. As noted in Sec. 4-10, for a single-particle orbital angular-momentum eigenfunction, the parity is determined by l, through the transformation properties of the spherical harmonics, to be $(-)^l$. If we combine a number of particles, there is no longer any such unique relation with the total orbital angular momentum L. Rather, the parity is given by $\prod_k (-)^{l_k}$, where l_k is the orbital angular momentum of the kth particle.

If we now introduce spin, this has no effect on these parity-build-up considerations. The spin, being an angular momentum, is an axial vector, with sense invariant under inversion. The intrinsic parity, which determines the change of sign of the spin *functions* (as opposed to the spin direction) under inversion, is arbitrary so long as no transmutation of particles is considered. We may take it to be even for electrons. Thus the parity of an atomic state is still determined only by the orbital part of the wavefunction. Concerning the representations for half-integral angular momenta, we see that we have the same double-valuedness as in the pure rotation group discussed earlier. This ambiguity of sign of the representation matrices, even for proper rotations, obscures the simple distinction of even and odd representations indicated in (5-85). However, by definition, this relation still must be valid if we restrict the rotation R to the unit operation so that only the inversion operation is involved.

It might appear that in the double-valued representations parity loses its significance because of the intrinsic sign ambiguity arising because of the sign change under a rotation by 2π. This is, of course, not true, as may be illustrated by considering the application of parity considerations in selection rules for dipole transitions. Since both initial- and final-state wavefunctions enter the matrix element together with the electric-dipole operator, a rotation by 2π leaves the matrix element unchanged whether the system has integral or half-integral angular momentum. However, inversion leaves it unchanged, and hence allowed to be nonvanishing, *only* if the initial and final states belong to representations of opposite parity.

5-16 Time-reversal Symmetry

The inclusion of inversion with the spatial rotations as a symmetry operation suggests through the relativistic equivalence of space and time that we also include a time-reversal operation T, which takes t into $-t$. Application of this operation classically requires reversing all velocities and letting time proceed in the reverse direction so that a system runs back through its past history. That this is a classically allowed symmetry follows from the fact that $\mathbf{F} = m\mathbf{a}$ involves only a *second* derivative with respect to time. A similar situation holds in quantum mechanics provided that H is real, as it is expected to be, since it represents an energy. If this is so, and if we momentarily neglect spin, T simply transforms ψ into ψ^*. We can see this by considering the time-dependent Schrodinger equation

$$H\psi = i\hbar\frac{\partial\psi}{\partial t}$$

If we take the complex conjugate and use the reality of H, we obtain

$$H\psi^* = i\hbar\frac{\partial\psi^*}{\partial(-t)}$$

Thus the state ψ^* will evolve into $+t$ in exactly the same way as ψ would have evolved in the $-t$ direction. Since probability density is proportional to $|\psi|^2$, it is unaffected by the operation. However, the momentum distribution, being proportional to the imaginary part of $\psi^*\nabla\psi$, is reversed, as it should be. If we are considering a stationary state, clearly its energy is unchanged, since $H\psi = E\psi$ implies $H\psi^* = E\psi^*$. There will or will not be a degeneracy associated with this symmetry, depending on whether the set of ψ^* is, or is not, linearly independent of the set of ψ corresponding to a given energy. In these considerations it must be kept in mind that any magnetic field present in H must be reversed in the time-reversal operation. This is taken care of automatically if the field is produced by part of the quantum-mechanical system under consideration, because a reversal of momenta reverses the field. However, if one is considering a system immersed in an external field, it must be explicitly reversed. For example, the wavefunction with $L_z = 1$, namely, $\psi \sim e^{i\varphi}$, goes into $\psi^* = e^{-i\varphi}$, with $L_z = -1$. In the absence of a magnetic field, this must have the same energy. In the presence of a field, the energy will remain the same, provided that the field is reversed when the transformation is made. If we had considered only an internal magnetic-dipolar interaction between two atoms, then T would have reversed both magnetic moments and the energy would be automatically unchanged.

It is important to note that T is not a linear and unitary operator as have been all our previous transformations. This is evident because $T(c\psi) = c^*(T\psi)$, whereas, under a unitary transformation, linearity would have required $T(c\psi) = c(T\psi)$. An operator with this property is said to be *antilinear*, and if it also conserves the magnitude of the scalar product so that

$$|(T\psi, T\varphi)| = |(\psi, \varphi)|$$

then it is called *antiunitary.*

Determination of the time-inversion operator. When we take spin into account, T is not simply the operation of complex conjugation as it is for a simple Schrödinger wavefunction as considered above. However, it *is* an antiunitary operator. This can be seen by noting that the time dependence of any energy eigenfunction is $e^{-iE_nt/\hbar}$, whether or not spin is involved. Hence, if several eigenfunctions of different energy are superposed, the time-dependent coefficient $c_n(t)$ must go into $c_n^*(t)$ if the direction of time is reversed. An antiunitary operator will make this transformation.

Now, the product of any two antiunitary operators, such as T and complex conjugation K, is evidently a unitary operator U.

$$TK = U$$

But in that case

$$T = UK \tag{5-86}$$

since K^2 is the identity. This result shows that the most general form T can take is the product of a unitary operator and the operation of complex conjugation. We can narrow this down by using the physical fact that $T^2\psi$ can differ from ψ by at most a constant factor of unit magnitude. Thus, in matrix notation,

$$\mathbf{T}^2 = \mathbf{UKUK} = \mathbf{UU}^* = c\mathbf{E} \tag{5-87}$$

where $\mathbf{E}$ is the unit matrix. Using the unitarity of $\mathbf{U}$, we have

$$\mathbf{U} = c(\mathbf{U}^*)^{-1} = c\tilde{\mathbf{U}}$$

Taking the transpose,

$$\tilde{\mathbf{U}} = c\mathbf{U} = c^2\tilde{\mathbf{U}}$$

Thus $c^2 = 1$, $c = \pm 1$, and the unitary matrix $\mathbf{U}$ must be either completely symmetric or antisymmetric on taking the transpose. Returning to (5-87), we see that it becomes

$$\mathbf{T}^2 = \pm\mathbf{E} \tag{5-88}$$

so that no possibility exists except that $T^2\psi = \pm\psi$. Clearly, when $T = K$ as for simple Schrodinger functions, $T^2 = E$. However, when there is an odd number of particles with half-integral spin, it turns out that the lower sign will hold.

To see that this is the case, we note that simple physical operators can be divided into two classes, those containing even powers of time, and those containing odd powers. The first class contains ordinary coordinate operators; the second contains linear and angular-momentum operators. Operators of the first sort will commute with T, for example,

$$T\mathbf{q} = \mathbf{q}T \tag{5-89a}$$

whereas those of the second sort will *anticommute*, for example,

$$T\mathbf{p} = -\mathbf{p}T \tag{5-89b}$$

Using the explicit forms $\mathbf{p} = (\hbar/i)\boldsymbol{\nabla}$ and $T = UK$, we can readily see that (5-89) implies that U commutes with multiplication by, and differentiation with respect to, the spatial coordinates and hence that U can have an effect only on the spin variables. We now determine U by observing that the spin components of each particle obey (5-89b). For example,

$$\mathbf{T}\mathbf{s}_{ix} = -\mathbf{s}_{ix}\mathbf{T} \tag{5-90}$$

where $i = 1, 2, \ldots, n$ runs over all particles. But the matrices of s_{ix} are all real. Hence

$$\mathbf{T}\mathbf{s}_{ix} = \mathbf{U}\mathbf{K}\mathbf{s}_{ix} = \mathbf{U}\mathbf{s}_{ix}\mathbf{K}$$

By using (5-90), this must equal $-\mathbf{s}_{ix}\mathbf{U}\mathbf{K}$. Hence $\mathbf{U}$ anticommutes with $\mathbf{s}_{ix}$. A similar argument holds for $\mathbf{s}_{iz}$, which is also real. However, since $\mathbf{s}_{iy}$ is purely imaginary, this argument shows that $\mathbf{U}$ *commutes* with $\mathbf{s}_{iy}$. These commutation properties of $\mathbf{U}$ immediately suggest that $\mathbf{U}$ be chosen as a simple product of Pauli matrices,

$$\mathbf{U} = \boldsymbol{\sigma}_{1y}\boldsymbol{\sigma}_{2y}\cdots\boldsymbol{\sigma}_{ny} \tag{5-91}$$

which satisfies all the requirements, including normalization. In fact it can be shown that, apart from a phase factor, this is a unique solution. Hence, we conclude that

$$\mathbf{T} = \boldsymbol{\sigma}_{1y}\boldsymbol{\sigma}_{2y}\cdots\boldsymbol{\sigma}_{\mathrm{n}y}\mathbf{K} \tag{5-92}$$

If we allow this operator to act on a state function, we have

$$T\psi(\mathbf{r}_1, \mu_1, \ldots, \mathbf{r}_n, \mu_n) = (-i)^{2(\mu_1+\cdots+\mu_n)}\psi(\mathbf{r}_1, -\mu_1, \ldots, \mathbf{r}_n, -\mu_n)^* \tag{5-93}$$

where μ_i is here used to denote the quantized z component $(\pm\frac{1}{2})$ of the ith spin. From this result it is evident that, if n is even, $(\mu_1 + \cdots + \mu_n)$ is integral and hence $T^2\psi = \psi$. However, if n is odd, we see that $T^2\psi = -\psi$, as indicated above.

Kramers' theorem. From this result we can immediately obtain the celebrated *Kramers' theorem.*[1] This states that all energy levels of a system containing an odd number of electrons must be at least doubly degenerate regardless of how low the symmetry is, provided that there are no magnetic fields present to remove time-reversal symmetry. This theorem follows from the fact that, if $T^2\psi = -\psi$, then $T\psi$ is orthogonal to ψ. Since $T\psi$ must also have the same energy as ψ, by time-reversal symmetry, at least this double degeneracy must exist. The orthogonality is proved by noting first that, for any functions ψ and φ, we have

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[1] H. A. Kramers, *Koninkl. Ned. Akad. Wetenschap., Proc.*, **33**, 959 (1930).

$$(T\psi, T\varphi) = (UK\psi, UK\varphi) = (K\psi, K\varphi) = (\psi, \varphi)^* = (\varphi, \psi) \tag{5-94}$$

Hence $$(T\psi, \psi) = (T\psi, T^2\psi) = (T\psi, -\psi) = -(T\psi, \psi)$$

and $(T\psi, \psi)$ must equal zero. Evidently the proof fails if there is an even number of electrons, so that $T^2\psi = \psi$, and in fact in this case no degeneracy need exist unless there is some spatial symmetry.

Representations and extra degeneracies. Because of the antiunitary nature of T, it is not possible to find a matrix representation in the usual sense for the group containing T and all the other antiunitary operators TR_i formed as products of T with ordinary unitary operators representing spatial coordinate transformations. However, we can still define matrices $D(TR_i)$ by

$$TR_i\psi_\kappa = \sum_\lambda \psi_\lambda D(TR_i)_{\lambda\kappa} \tag{5-95}$$

because the transformed eigenfunction must still be expressible as a linear combination of the degenerate set of partners ψ_λ. Moreover, these matrices are unitary, on the assumption that the ψ_λ are chosen to be orthogonal. The proof goes exactly as the analogous one in Sec. 3-6, by using (5-94). The difficulty that arises is that, e.g.,

$$D(TR_iR_j) = D(TR_i)D(R_j)^* \neq D(TR_i)D(R_j) \tag{5-96}$$

This difficulty is fundamental and ineradicable. Accordingly, Wigner[1] introduces the nomenclature *corepresentations* for these matrix systems which arise when a group containing antiunitary as well as unitary operations is under consideration.

Without going into this problem in detail, we can make considerable progress by noting that given a set of degenerate partners $\psi_\kappa^{(j)}$, arising from spatial symmetry, which form a basis for a representation $D^{(j)}(R)$, we can form a new set of degenerate functions $T\psi_\kappa^{(j)} = \bar{\psi}_\kappa^{(j)}$. Under spatial transformations, these new functions transform according to $D^{(j)}(R)^*$. This is readily seen by considering

$$\begin{aligned} R\bar{\psi}_\kappa^{(j)} &= RT\psi_\kappa^{(j)} = TR\psi_\kappa^{(j)} = T\sum_\lambda \psi_\lambda^{(j)} D^{(j)}(R)_{\lambda\kappa} \\ &= \sum_\lambda (T\psi_\lambda^{(j)}) D^{(j)}(R)^*_{\lambda\kappa} \\ &= \sum_\lambda \bar{\psi}_\lambda^{(j)} D^{(j)}(R)^*_{\lambda\kappa} \end{aligned} \tag{5-97}$$

where we have used the fact that time reversal commutes with any ordinary coordinate transformation.

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[1] Wigner, *op. cit.*, chap. 26.

The question then arises whether or not any new degeneracy is brought in by the time-reversal symmetry, i.e., whether the $\bar{\psi}_\lambda^{(j)}$ are linearly independent of the $\psi_\lambda^{(j)}$. Wigner has shown[1] that this question can be resolved by consideration of the representation matrices **D** and **D*** (for the operations R alone, without considering the antiunitary operations). Three cases arise:

a. **D** and **D*** are equivalent to the same real irreducible representation.
b. **D** and **D*** are inequivalent.
c. **D** and **D*** are equivalent but cannot be made real.

The results also depend on whether we have integral or half-integral spin. We consider first the case of integral spin, so that $T^2 = +1$.

In case *a*, we can imagine that a suitable transformation has been carried out so that $\mathbf{D}(R) = \mathbf{D}(R)^* =$ real for both the ψ_λ and $\bar{\psi}_\lambda$. The same $D(R)$ will also hold for the real functions $u_\lambda = (\psi_\lambda + \bar{\psi}_\lambda)$ and $v_\lambda = i(\psi_\lambda - \bar{\psi}_\lambda)$. But because of their reality, no symmetry operation, *including T*, will mix any of the u's with the v's. Thus the u's or v's alone each form a basis for the same representation of the total symmetry. Since the two sets have the same energy, they must be identical, barring *accidental* degeneracy. Thus, in this case, no new degeneracy is introduced by time reversal symmetry.

In case *b*, since **D** and **D*** are inequivalent representations, the $\bar{\psi}_\lambda$ and ψ_μ are all mutually orthogonal; yet both sets are required together to represent the full symmetry of the group. Hence the degeneracy is doubled by the presence of time-reversal symmetry.

In case *c*, since **D** and **D*** cannot be made real, it follows that the ψ_λ and $\bar{\psi}_\lambda$ cannot be made real, since if they were,

$$D(R)_{\mu\lambda} = (\psi_\mu, P_R\psi_\lambda)$$

would also be real for all members of the group of spatial operations. But if the ψ_λ and $\bar{\psi}_\lambda$ cannot be made real, then both these independent functions are required in the basis for the full group including T and the degeneracy is doubled.

Now, let us consider the case of half-integral spin, where $T^2 = -1$. In case *a*, if we proceed as above, the proof fails because, with $T^2 = -1$,

$$Tu_\lambda = iv_\lambda \qquad Tv_\lambda = -iu_\lambda$$

so that time reversal mixes the u's and v's just as effectively as it does the ψ's and $\bar{\psi}$'s. Thus, both are required, and the degeneracy is doubled. For case *b*, the argument goes through as above, and the degeneracy is doubled. For case *c*, the argument is rather more lengthy, and we shall simply state Wigner's result that there is no extra degeneracy.

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[1] E. P. Wigner, *Göttingen Nachrichten, Math.-Physik. Kl.*, p. 546, 1932.

The above results are made easier to apply by using a criterion due to Frobenius and Schur[1] which allows cases a, b, and c to be distinguished with only the character table and the diagonal elements of the group-multiplication table known. The test is as follows: Form the sum of the characters of the squares of all h group elements. This sum has the value h, 0, or $-h$, according as we are dealing with cases a, b, or c. That is,

$$\sum_R \chi^{(j)}(R^2) = \begin{cases} h & \text{case } a \\ 0 & \text{case } b \\ -h & \text{case } c \end{cases} \tag{5-98}$$

We prove this result using the great orthogonality theorem, Eq. (3-8). In all cases,

$$\sum_R \chi^{(j)}(R^2) = \sum_R \sum_{\mu,\lambda} D^{(j)}(R)_{\mu\lambda} D^{(j)}(R)_{\lambda\mu}$$

In case a, where $\mathbf{D}^{(j)} = \mathbf{D}^{(j)*}$, this becomes, by using (3-8),

$$\sum_R \chi^{(j)}(R^2) = \sum_{\mu,\lambda} \sum_R D^{(j)}(R)^*_{\mu\lambda} D^{(j)}(R)_{\lambda\mu} = \sum_{\mu\lambda} \delta_{\mu\lambda} \frac{h}{l_j} = h$$

In case b, where $D^{(j)}$ and $D^{(j)*}$ are inequivalent, we can set $D^{(j)} = D^{(k)*}$, where $D^{(k)}$ is not related to $D^{(j)}$. But then the orthogonality theorem leads to zero. In case c, we have $\mathbf{D}^* = \mathbf{S}\mathbf{D}\mathbf{S}^{-1}$. Using this, with the orthogonality theorem, leads to

$$\sum_R \chi^{(j)}(R^2) = \frac{h}{l_j} \operatorname{Tr}(\mathbf{S}^*\mathbf{S})$$

Table 5-4

Effect of time-reversal symmetry on degeneracy

Case	*Frobenius-Schur test* $\sum_R \chi(R^2)$	*Relation between D and D**	*Integral spin*	*Half-integral spin*
a	h	D, D^* can be made real and equal	No extra degeneracy	Doubled degeneracy
b	0	D, D^* are inequivalent	Doubled degeneracy	Doubled degeneracy
c	$-h$	D, D^* are equivalent, but cannot be made real	Doubled degeneracy	No extra degeneracy

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[1] Frobenius and Schur, *Berl. Ber.*, p. 186, 1906.

It can be shown that $\mathbf{S}$ must be antisymmetric ($\mathbf{S} = -\tilde{\mathbf{S}}$) if $\mathbf{D}$ cannot be made real. Then $\mathbf{S}^* = -\mathbf{S}^{-1}$, and $\mathrm{Tr}\,(\mathbf{S}^*\mathbf{S}) = -l_j$. Thus

$$\sum_R \chi^{(j)}(R^2) = -h$$

as was to be shown.

The results of this section are summarized in Table 5-4. It might be remarked that time-reversal symmetry gives no additional degeneracy at all when the symmetry is the full rotation group. However, it becomes an important symmetry property in systems such as molecules or crystals with relatively low symmetry. For example, in the point group C_3, we have the character table

C_3	E	C_3	C_3^2
A	1	1	1
$E\left\{\right.$	1	ω	ω^2
	1	ω^2	ω

$\omega = e^{2\pi i/3}$

In the absence of time-reversal symmetry the two lower lines would form distinct one-dimensional representations, with $\sum_R \chi(R^2) = 1 + \omega + \omega^2 = 0$. However, since time reversal exists, they must be degenerate and hence they are conventionally lumped together as a two-dimensional representation E, despite the fact that no spatial operator in the group C_3 will transform a function from one line to the other.

5-17 More General Invariances

The rotation group, plus space and time inversion, is as much of the atomic symmetry as we shall consider in any detail. Further symmetries exist, however, and we shall now sketch the general situation of which these particular symmetries form an important part. The interest in this question arises from the intimate relation between symmetry properties and conservation laws. If the Hamiltonian of a system is invariant under a set of mutually commuting coordinate transformations R_i, this means that we can have simultaneously sharp values for the conjugate momenta. For example, we have already noted that the linear momentum $\mathbf{p}$ is best defined as that quantity which is "conserved," is a "constant of the motion," or is a "good quantum number" if H has translational invariance. Similarly, invariance under rotation leads to the conservation of angular momentum, invariance under translation in time to energy conservation, invariance under space inversion to parity conservation, and so on. Thus it is worthwhile to seek out the full symmetry of the problem.

In addition to the coordinate transformations mentioned above, the theory of relativity states that all nonaccelerated frames of reference are equivalent. In other words, H must be invariant under any proper Lorentz transformation, these forming the *Lorentz group.* Such a transformation can be viewed geometrically as a rotation through a complex angle in the four-dimensional space with coordinates $(x, y, z, \tau = ict)$. For example, if there is a relative velocity $v = \beta c$ along x, then the rotation is in the $x\tau$ plane and the transformation equations are

$$\begin{aligned} x' &= \gamma x - i\beta\gamma\tau = x\cos\theta - \tau\sin\theta \\ y' &= y \\ z' &= z \\ \tau' &= \gamma\tau + i\beta\gamma x = x\sin\theta + \tau\cos\theta \end{aligned} \tag{5-99}$$

where $\gamma = (1 - \beta^2)^{-\frac{1}{2}}$ and $\tan\theta = i\beta$, or $\theta = i\tanh^{-1}\beta$. Such a rotation leaves the length $(x^2 + y^2 + z^2 - c^2t^2)^{\frac{1}{2}}$ invariant. If we combine this Lorentz group with the translations in space and time, we have what is known as the *proper Poincaré group.* If, in addition, we add the space and time inversions, we have the *unrestricted Poincaré group.*

To conclude the list of possible invariances, we mention charge conjugation C. This operation replaces each elementary particle by its antiparticle but leaves the space-time degrees of freedom unchanged. All the operators i, C, T commute with each other and with the Lorentz group $\mathscr{L}$. Thus we can represent the presumed total symmetry (apart from the translations, which just assure momentum and energy conservation) as the direct product of the continuous group $\mathscr{L}$ with the discrete Abelian group E, i, C, T, iC, iT, CT, iCT.

In discussing invariances of this sort, it is worthwhile to distinguish between two different levels of generality. As long as the discussion is confined to some specific concrete Hamiltonian, one can make definite statements. For example, if all the terms representing both internal interactions and externally applied fields have inversion symmetry, parity is rigorously a good quantum number in the formal problem to be solved. If one then applies a perturbation such as an electric field which destroys the inversion symmetry, parity fails as a quantum number and matrix elements coupling odd and even states exist. The extent of the breakdown will be determined by the relative strength of the nonsymmetric interaction and the energetic separation of states of opposite parity under the symmetric part of the Hamiltonian. If these should lie close together or actually be degenerate, then the breakdown of parity would be large. This accounts for the first-order Stark effect in the $n = 2$ state of hydrogen, in the approximation that the $2s$ and $2p$ levels are treated as degenerate.

The basic questions of recent interest are on the more general level. In this case, the symmetry operation is applied to all of nature. This eliminates all "external" interactions and leaves only the "internal" interactions specified by fundamental physical laws. Then we are asking: (1) Would a possible physical world with the same physical laws be the result of inverting all coordinates through some arbitrary origin, thus transforming a world of right-handed systems into left-handed ones? (2) Would a possible world result if all velocities were reversed (including currents producing magnetic fields, etc.) and time were allowed to develop in the reverse sense? (3) Would a possible world result if all particles were transformed to antiparticles?

Until 1956, it had been thought likely that the answers to all these questions were affirmative. In that year, however, Lee and Yang noted[1] that there was no good evidence for parity conservation in the nuclear processes involving weak interactions, and in fact some evidence against it. They proposed further experimental tests, which, when carried out,[2] showed conclusively that parity is not conserved in the β decay of nuclei nor in the decay of π mesons. Thus we are forced to conclude that, in addition to the usual scalar terms in the Hamiltonian, there must also be pseudoscalar terms which change sign even when *all* coordinates are inverted. The experimental situation is perhaps most easily understood in the β-decay experiment of Wu et al. The crucial experimentally observed fact is that the direction of a polar vector (the velocity $\mathbf{v}$ of the emitted β particles) is determined by the sense of an axial vector (the magnetic field $\mathbf{H}$, which polarizes the nuclei). Since inversion leaves $\mathbf{H}$ unchanged, while reversing $\mathbf{v}$, the fact is inconsistent with universal inversion symmetry.

It has been suggested[3] that the situation might best be handled by dropping inversion and charge conjugation as separate symmetry operators, retaining only their product iC as a form of generalized inversion. In the experiment cited, this would now cause $\mathbf{H}$ to reverse, since positrons would now be carrying the current in the magnet, and the antinuclei would emit anti-β particles in the same direction as the normal particles had been before. This would remove the contradiction. The directions of the various vectors involved are illustrated schematically in Fig. 5-6. This suggestion is welcome because of the Schwinger-Lüders-Pauli theorem.[4] This shows that, under very general assumptions, the product iCT should be a valid symmetry operation in any local field theory. Thus, if T is an allowed operation, iC must also be one. Since the reduced group E, iC, T, iCT is isomorphic with the group E,

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[1] T. D. Lee and C. N. Yang, *Phys. Rev.*, **104**, 254 (1956).

[2] C. S. Wu, E. Ambler, R. W. Hayward, D. D. Hoppes, and R. P. Hudson, *Phys. Rev.*, **105**, 1413 (1957); R. L. Garwin, L. M. Lederman, and M. Weinrich, *Phys. Rev.*, **105**, 1415 (1957).

[3] E. P. Wigner, *Revs. Modern Phys.*, **29**, 255 (1957).

[4] See, for example, G. Lüders, *Kgl. Danske Videnskab. Selskab Mat.-fys. Medd.*, **28** (5), 1954.

i, *T*, *iT*, it forms a group isomorphic with the unrestricted Poincare group when combined with the Lorentz group and the translations. However, th apparent necessity of joining *C* to *i* to form an allowed symmetry operat is initially a bit unsettling because of all the evidence in favor of the simpl

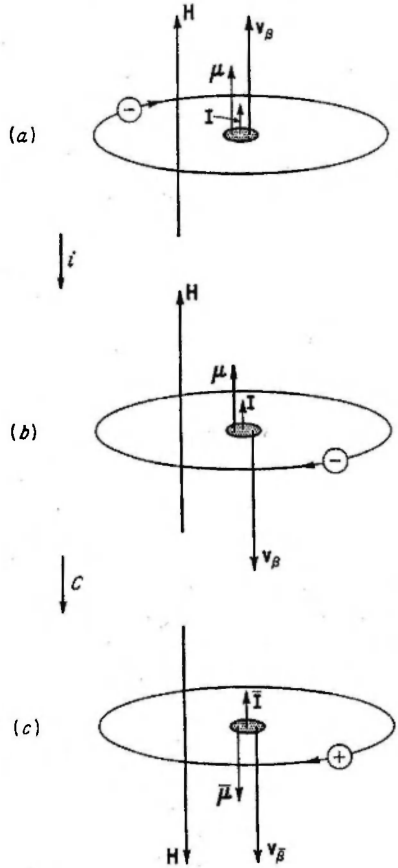

Fig. 5-6. *Schematic diagram of β-de experiment of Wu et al., showing eff of successive application of i and C o ators. Figure shows current circulat in magnet to produce field* **H** *which o ents magnetic moment* **μ** *of nucleus, w associated angular momentum* **I**, *and a the velocity* $\mathbf{v}_\beta$ *of the emitted β- parti Arrangement (b) is not observed, tho (a) is. Hence i is not a symmetry o ation.*

i operator. This situation illustrates the fact that great and effective can be made of symmetry properties which are not ultimately accurate *all* types of forces. So long as the property holds for all the forces play a significant role in a process, the corresponding conservation law will well obeyed. In general, as one considers weaker and weaker forces, residual symmetry group will tend to decrease. In the last analysis, o experimental investigation can provide us with the knowledge of what sy metry actually exists in nature.

EXERCISES

5-1 Use the fact that we can write $J = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}$, where φ is the angle of rotation about the axis of J, to show that

$$P_\theta\psi(\varphi) = e^{-i\theta J/\hbar}\psi(\varphi) = \psi(\varphi - \theta)$$

5-2 Simplify the general formula for $D^{(j)}_{m'm}(\alpha, \beta, \gamma)$ to that for $D^{(j)}_{m'j}(\alpha, \beta, \gamma)$. Using this simplified formula, work out all the coefficients $D^{(2)}_{m'2}(\alpha, \beta, \gamma)$.

5-3 When one measures the component of a magnetic moment along a magnetic field in a Stern-Gerlach type of experiment, one forces a system to give a sharp value to the component of angular momentum in that direction. The probability of finding any given value of m is just $|c_m|^2$, where $\psi = \sum\limits_m c_m\psi_m{}^{(j)}$, and the z axis is the axis of the field. Assume that the fields in two successive experiments on the same atoms are inclined at an angle θ. (*a*) What is the probability as a function of θ that an atom which was in state m in the first experiment will be found in state m' in the second experiment for arbitrary j? (You may assume that the wavefunction does not change in passing from one experiment to the next.) (*b*) Tabulate explicit answers for the cases $j = 0, \frac{1}{2}$, and 1. (*c*) Finally, specialize these matrices for $\theta = \pi/2$.

5-4 A spinor is said to point in the z direction if $\psi = e^{i\delta}u_+$, where $u_+ = \begin{pmatrix}1\\0\end{pmatrix}$ and δ is any real number, so that J_z is certainly $+\frac{1}{2}$. (*a*) Using this definition and the representation $D^{(\frac{1}{2})}$ of the rotation group, in what direction is the spinor $\psi' = a_-u_- + a_+u_+ = \begin{pmatrix}a_+\\a_-\end{pmatrix}$ pointing? ($|a_+|^2 + |a_-|^2 = 1$.) Specify the direction by giving the polar and azimuthal angles θ and φ. (*b*) What are a_+ and a_- for a spinor pointing in the x direction and the y direction? Remember that a_+ and a_- are determined only within a common phase factor.

5-5 Write down the specific transformation matrices for single rotations through angle θ of spinors ($j = \frac{1}{2}$) about the y and z axes. Work out the transformation matrix for a rotation θ about the x axis, using the general result for $D^{(\frac{1}{2})}(\alpha, \beta, \gamma)$. Using these results, note that rotating a *spinor* u_+ by π about x and about y leads to spinors of different phase. Use $D^{(1)}(\alpha, \beta, \gamma)$ to show that rotating a z-directed *vector* $\psi_z = \psi\,(j = 1, m = 0)$ in the same way leads to no phase difference.

5-6 Use the Wigner coefficients to express the wavefunction of an atomic state with $L = 2, S = 2, J = 0$ in terms of products of orbital and spin functions having $L = 2$ and $S = 2$, respectively. What is the probability that $S_z = 2$ in this state?

5-7 Consider the state $l = 1$, $s = \frac{1}{2}$, $j = \frac{1}{2}$, $j_z = m$. (*a*) Show that the charge distribution is spherically symmetric. (*b*) Find the spatial distribution of spin direction for the state $m = +\frac{1}{2}$. (Spin direction is defined as the direction ζ along which S_ζ is certainly $+\frac{1}{2}$.) Make a simple sketch showing your results in the xz plane.

5-8 The Landé g factor of a state is defined as

$$g = \frac{\mu_z}{\beta M} = \frac{(JM\,|2S_z + L_z|\,JM)}{(JM\,|S_z + L_z|\,JM)} = \frac{(JM\,|2S_z + L_z|\,JM)}{M} = 1 + \frac{(JM\,|S_z|\,JM)}{M}$$

Using the Wigner coefficients to express ψ_{JM} in terms of eigenfunctions of S_z ar L_z, evaluate g for the case $S = \frac{1}{2}$ and general L. Show that your result is in agre ment with that calculated for this case using the vector model of elementar physics. [See Eq. (6-65).]

5-9 (*a*) Calculate the relative intensities of all possible π ($\Delta M = 0$) and ($\Delta M = \pm 1$) Zeeman components (in a weak magnetic field) for the transitio between a $^2S_{\frac{1}{2}}$ and a $^2P_{\frac{3}{2}}$ state. In this calculation assume linear polarizatio along x and z for σ and π transitions, respectively. (*b*) Using the g factors com puted in Exercise 5-8 to determine the energy differences, prepare a diagra showing the splitting and intensity pattern which would be observed. Label al the lines, and distinguish the σ and π transitions.

5-10 Consider the many-electron electronic spin-spin interaction. Note th in general this can be decomposed into a sum of irreducible tensor operators a indicated for the case of two spins in Eq. (5-65). Consider a system perturb from spherical symmetry to only axial symmetry, which is in a Σ state. That i the orbital wavefunction is invariant under rotation of coordinates about the axi If the system has an electronic spin S, which is an approximately good quantu number because the axial perturbation is small compared with energy differenc to states of different S, use the Wigner-Eckart theorem to show that the spin-spi interaction produces energy splittings within this state (i.e., diagonal in S) equivale to those produced by the effective Hamiltonian

$$H = D[3S_z^2 - S(S + 1)] \qquad D = \text{constant}$$

operating on the total-spin state functions. This effect gives rise to the fin structure splitting of the ^6S Mn^{++} paramagnetic-resonance spectrum in an axi crystal field. It also produces the large term ($\sim 2\ \text{cm}^{-1}$) coupling the spin to t figure axis in the $^3\Sigma$ ground state of O_2. (HINT: This problem requires som physical thought, but not a great deal of mathematical manipulation.)

5-11 Use the Wigner-Eckart theorem and the Racah coefficients to work o an explicit expression for the matrix elements of the form

$$(j_1, j_2, J - 1, M\,|j_{1z}|\,j_1, j_2, J, M)$$

where j_1 and j_2 have been coupled to form J and $J - 1$ in the initial and fin states, respectively.

5-12 (*a*) Classify the following as to whether they transform as (polar) vecto or as pseudovectors (axial vectors), i.e., whether they do or do not change si under the inversion operator ($\mathbf{r}' = -\mathbf{r}$): velocity, momentum, grad, angul momentum, force, electric field, magnetic field, magnetic vector potential, magne moment. (*b*) Show that the Hamiltonian for an atom is invariant under inversi when it includes the Coulomb interaction among electrons and nucleus, spi orbit coupling (taken in the form $\lambda\,\Sigma\,\mathbf{l}_i \cdot \mathbf{s}_i$), spin-spin coupling [as in Eq. (5-65)], a the interaction with a uniform magnetic field. Hence deduce that parity is exact quantum number for describing the state of an atom under these conditio (*c*) Would this conclusion be true if the spin-orbit coupling took the form $\lambda \sum_i \mathbf{r}_i \cdot \mathbf{s}_i$? Explain.

5-13 Classify the operators listed in Exercise 5-12*a* according to whether they are even or odd under time inversion (including time inversion of sources of any fields).

5-14 The 2 $^2S_{\frac{1}{2}}$ state of atomic H is metastable since dipole transitions to the ground state (1 $^2S_{\frac{1}{2}}$) are forbidden by the parity rule. How intense must a perturbing static electric field be to reduce the lifetime of the metastable state to 10^{-8} sec? [HELPFUL INFORMATION: In the absence of external fields the 2 $^2S_{\frac{1}{2}}$ state lies 1,058 Mc/sec above the 2 $^2P_{\frac{1}{2}}$ state because of the Lamb shift. For simplicity, you may ignore the nearby 2 $^2P_{\frac{3}{2}}$ state. The general expression for transition probability per unit time[1] via electric dipole transitions is

$$w = \frac{4e^2\omega_{kn}{}^3\,|\mathbf{r}_{kn}|^2}{3\hbar c^3}$$

This effect of an electric field is called "quenching" of metastables.]

REFERENCES

CONDON, E. U., and G. H. SHORTLEY: "The Theory of Atomic Spectra," chap. III, Cambridge University Press, New York, 1951.
EDMONDS, A. R.: "Angular Momentum in Quantum Mechanics," Princeton University Press, Princeton, N.J., 1957.
FANO, U., and G. RACAH: "Irreducible Tensorial Sets," Academic Press Inc., New York, 1959.
ROSE, M. E.: "Elementary Theory of Angular Momentum," John Wiley & Sons, Inc., New York, 1957.
ROTENBERG, M., R. BIVINS, N. METROPOLIS, and J. K. WOOTEN, Jr.: "The 3-*j* and 6-*j* Symbols," Technology Press, Cambridge, Mass., 1959.
WIGNER, E. P.: "Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra," Academic Press Inc., New York, 1959.

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[1] L. I. Schiff, "Quantum Mechanics," 2d ed., p. 261, McGraw-Hill Book Company, Inc., New York, 1955.

6

QUANTUM MECHANICS OF ATOMS

We now turn back from the development of group-theoretical method to our basic objective, namely, the calculation of the properties of atom molecules, and solids by quantum-mechanical means. Henceforth th group theory will be brought to bear when helpful, but our central objectiv is to formulate a quantitative understanding of these physical system rather than simply to illustrate one particular theoretical tool.

Although there are similarities in the theory of atoms and of molecule the calculations in the two cases differ sufficiently so that we shall first concentrate on the simpler atomic problem. Here we have a single massiv positive nucleus providing a central force center. This results in a Hamiltonian with overall spherical symmetry, which allows great simplificatio Before plunging into detailed calculations, let us briefly review the element of atomic structure so that we may see just what we are trying to calcula more quantitatively.

6-1 Review of Elementary Atomic Structure and Nomenclature

To specify the quantum state of an atom, we first specify the *configuration*. This tells us which one-electron central-field eigenstates (labeled by n and l) are occupied. For example, the ground state of the silicon atom ($Z = 14$) has the configuration $1s^22s^22p^63s^23p^2$. Since the electrons interact among themselves, the energy of the atom is not determined by this much information alone. We must also know how the various one-electron functions are coupled together to form eigenfunctions for the entire atom. For this purpose we can neglect the closed shells, since there is no freedom left if all states are occupied. Thus in our example, we concentrate on the $3p^2$ part. Applying our vector-model result to the orbital eigenfunctions,

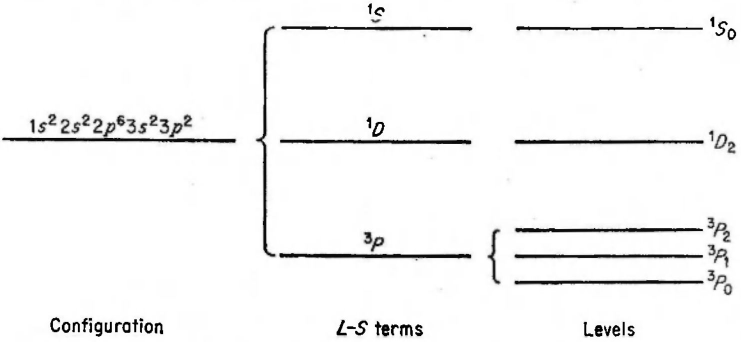

Fig. 6-1. *Hierarchy of levels for the ground configuration of silicon.*

$$D^{(1)} \times D^{(1)} = D^{(0)} + D^{(1)} + D^{(2)} = S + P + D$$

while for the spins

$$D^{(\frac{1}{2})} \times D^{(\frac{1}{2})} = D^{(0)} + D^{(1)}$$

Thus two p electrons can form the following *L-S terms*: $^1S, {}^1P, {}^1D, {}^3S, {}^3P, {}^3D$. Later we shall see how the Pauli principle excludes all except $^3P, {}^1S, {}^1D$ if the electrons are *equivalent* (same n and l), as in this example. The Wigner coefficients could be used to express the eigenfunctions of L, M_L in terms of those of l_1, m_1 and l_2, m_2, for example. These L-S terms differ in energy by the order of an intra-atomic Coulomb energy, i.e., typically a few electron volts.

Finally we introduce the small magnetic energies referred to as the spin-orbit coupling and decompose the L-S terms into individual *levels* of definite total angular momentum J. The various levels of a given term form its *multiplet structure*. The intervals in the multiplet are of order $(v/c)^2 \sim (Z_{\text{eff}}/137)^2(l/n^2)$ less than the Coulomb energies, namely, of order 1 to 1,000 cm^{-1}. This hierarchy of level structure may be depicted schematically as shown in Fig. 6-1. The individual levels are $(2J + 1)$-fold degenerate, and these sets of degenerate functions form bases for irreducible representatio of the full rotation group of the whole system as a unit. Since the Ham tonian is rigorously invariant under such rotations, these degeneracies exact to all orders of approximation so long as no external fields are appli to disturb the isotropy of space. In other words, J is rigorously a go quantum number. This is *not* true of the one-electron quantum numb which enter the configuration labels, since the Hamiltonian is not invari under a rotation of the coordinates of one particle. In fact, the Wign coefficients prescribe what linear combinations of one-electron functio form these proper eigenfunctions. In the *L-S* coupling approximation, th prescription would be carried out in stages: first coupling $\mathbf{l}_1 + \mathbf{l}_2 = \mathbf{L}$ ar $\mathbf{s}_1 + \mathbf{s}_2 = \mathbf{S}$; then coupling $\mathbf{L} + \mathbf{S} = \mathbf{J}$.

The three *Hund rules* determine the ground state of an atom who configuration is given. These rules dictate that to find the ground state:

1. Choose the maximum value of S consistent with the Pauli princip

2. Choose the maximum value of L consistent with the Pauli princip and rule 1.

3a. If the shell is less than half full, choose $J = J_{\text{min}} = |L - S|$.

3b. If the shell is more than half full, choose $J = J_{\text{max}} = L + S$.

Applying these rules to the Si example, we find that the ground state is ^3P as shown in the diagram above. Although we shall examine these resul more closely later on, it is probably worth emphasizing right here tha despite its appearance, rule 1 has nothing to do with a magnetic couplin between spins. Rather it arises from the antisymmetry of the wavefunctio This keeps electrons with parallel spins out of each other's way, thus lowerin the *electrostatic-repulsion energy*. Only rule 3 is based on magnet energies.

If we consider heavy atoms where Z is high, v/c becomes larger and th magnetic forces become much more important. In this limiting case, th concept of *L-S* terms is not very useful. Instead we couple the spin of eac electron to its own orbital motion forming a resultant j_i. We then specif a level by quoting all the j_i's and the total J which they form by vect addition. Of course J is a rigorous quantum number in this *j-j couplin* scheme, just as with *L-S* coupling. We shall confine our attention largel to the *L-S* coupling case, which pertains to the more common light atom

If high accuracy is required, one cannot ignore the admixture of con figurations other than the nominal one by the nonspherical part of the on electron Hamiltonian. This part arises, for example, when electrons oth than the one under consideration are present outside closed shells. Th admixture is called *configuration interaction*, and it is usually ignored approximate work. If it is taken into account, we are at least assured th complete accuracy can be obtained if enough configurations are included because the set of all configurations forms a complete orthogonal set. Convergence in this method of *superposition of configurations* is often rather slow, however.

6-2 The Hamiltonian

We shall usually confine our attention to the approximate Hamiltonian

$$H = \sum_{i=1}^{N} \left[\frac{\mathbf{p}_i^2}{2m} - \frac{Ze^2}{r_i} + \xi(r_i)\mathbf{l}_i \cdot \mathbf{s}_i \right] + \sum_{i>j} \frac{e^2}{r_{ij}} \tag{6-1}$$

As will be discussed later, the spin-orbit coupling may be handled approximately by the term in $\xi(r) = (2m^2c^2r)^{-1}(\partial U/\partial r)$, where $U(r)$ is a spherically symmetric approximation to the potential inside the atom. We neglect all other magnetic and relativistic effects, hyperfine structure, etc., for the present. In fact, even (6-1) is too difficult to handle all at once; so we separate a simple spherically symmetric term H_0 and treat the rest as a perturbation H'. Thus

$$H_0 = \sum_i \left[\frac{\mathbf{p}_i^2}{2m} + U(r_i) \right]$$

and

$$H' = \sum_i \left[\sum_{j>i} \frac{e^2}{r_{ij}} - \frac{Ze^2}{r_i} - U(r_i) \right] + \sum_i \xi(r_i)\mathbf{l}_i \cdot \mathbf{s}_i \tag{6-2}$$

The physical idea of H_0 is that we consider each electron to move in $U(r_i)$, the Coulomb field of the nucleus as "screened" by the other electrons. For very small r, $U(r) \approx -Ze^2/r$, but for large r, the potential is much weaker, more like simply $-e^2/r$ in a neutral atom. By restricting U to the spherical form, we assure the separation of variables, and each electron will have a well-defined angular momentum, as assumed in the simple configuration labels. All that remains to be found is the radial dependence of the individual eigenfunctions. After this has been done, one introduces the first part of H' to split apart the L-S terms and then the second part to produce the multiplet structure.

6-3 Approximate Eigenfunctions

Simple approximate eigenfunctions. The simplest approximation is to assume *hydrogenic functions*. These differ from the hydrogen eigenfunctions only by the replacement of the nuclear charge by $(Z - s)$, where s is the screening charge of the inner electrons. Slater[1] has proposed a simple rule for choosing s. He assumes that each electron in the same shell as the one under consideration contributes 0.35 to s; each electron in the next in shell contributes 0.85; each electron in still lower shells contributes a 1.00 to the shielding. This leads to fair results but suffers from the convenience that the functions for the various shells are not orthogonal sin they are solutions for Hamiltonians with different potentials.

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[1] J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

A more systematic approach for the light atoms is to choose a sim form for each radial function and then to choose the best values for para eters entering the function by the variational method of minimizi the total energy. The method was introduced by Morse, Young, a Haurwitz,[1] extended by Duncanson and Coulson,[2] and recently carri further by machine computation by Tubis.[3] The assumed functions are

$$
\begin{aligned}
u(1s) &= \left(\frac{u^3a^3}{\pi}\right)^{\frac{1}{2}} e^{-uar} \\
u(2s) &= \left(\frac{u^5}{3\pi N}\right)^{\frac{1}{2}} \left[re^{-ur} - 3\left(\frac{A}{u}\right)e^{-ubr} \right] \\
u(2p_0) &= \left(\frac{u^5c^5}{\pi}\right)^{\frac{1}{2}} r \cos\theta e^{-ucr} \\
u(2p_{\pm 1}) &= \left(\frac{u^5c^5}{2\pi}\right)^{\frac{1}{2}} r \sin\theta e^{\pm i\varphi} e^{-ucr}
\end{aligned}
\tag*{(6-3}
$$

where $A = (a+b)^3/(1+a)^4$ is chosen for orthogonality of $u(1s)$ and $u(2s)$ The normalization constant N has the value $N = 1 - [48A/(1+b)^4] +$ $3A^2/b^2$. Within this framework, the values of the parameters a, b, c, and are determined and tabulated for all atoms up to 10 electrons. These calculations are actually made including the nonspherical part of the Hamiltonian, so that the L-S terms have distinct energies. Results are usually quoted for two low-lying L-S terms. These functions are quite useful for semiquantitative calculations.

More accurate variational eigenfunctions. We have just mentioned the use of a variational method to obtain approximate eigenfunctions. This method is based on the fact that the Schrödinger equation is the Euler equation which results when the calculus of variations is applied to finding the function ψ which minimizes $E = \int \psi^* H \psi \, d\tau$ subject to the constraint that the normalization integral $\int \psi^* \psi \, d\tau$ be held constant.[4] Therefore the exact solution of the Schrödinger equation for the ground state is precisely the function giving the absolute minimum energy. In any case, since the energy is stationary with respect to small changes in ψ about any eigenfunction, quite good energy eigenvalues may be obtained by using only moderately good approximate eigenfunctions. Moreover, we always get an upper bound for the ground-state energy and a simple analytic criterion for choosing the "best" approximate ψ within a class of functions such as those considered above. To get better eigenfunctions, one then must generalize the class of functions to which the variation method is applied by increasing the number of free parameters.

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[1] P. M. Morse, L. A. Young, and E. Haurwitz, *Phys. Rev.*, **48**, 948 (1935).

[2] W. E. Duncanson and C. A. Coulson, *Proc. Roy. Soc. Edinburgh*, **62**, 37 (1944).

[3] A. Tubis, *Phys. Rev.*, **102**, 1049 (1956).

[4] See, for example, H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," 1st ed., p. 208, D. Van Nostrand Company, Inc., Princeton, N.J., 1943.

This approach has been carried particularly far for the normal state of He, which is the simplest atomic problem which is not soluble exactly. Hylleraas[1] carried this through using about 10 parameters and including terms depending explicitly on r_{12} to represent the correlation of the two electrons. He managed to get an energy 24 cm^{-1} *below* the experimental energy of $-198{,}310.5\ \text{cm}^{-1}$. This apparent contradiction of the variational theorem is a consequence of neglect of relativistic and other higher corrections in the Hamiltonian. When these are inserted, the agreement is satisfactory. More recently, Kinoshita[2] has carried out a 39-parameter variational calculation of the nonrelativistic problem and made more careful allowance for the relativistic and quantum electrodynamic (Lamb-shift) effects. The most exhaustive calculation is that of Pekeris,[3] who used more than 200 terms and obtained an accuracy estimated to be 0.01 cm^{-1}, an order of magnitude better than the experimental value. This makes it pretty clear that no important errors remain in the Hamiltonian and that excellent results can be obtained by this method if one pushes it far enough. The method is not very practical for the heavier atoms with more electrons, however.

Hartree functions. A very reasonable type of approximate function was chosen by Hartree, namely,

$$\psi(\mathbf{r}_1, s_1, \ldots, \mathbf{r}_N, s_N) = u_1(\mathbf{r}_1)\chi_1(s_1) \cdots u_N(\mathbf{r}_N)\chi_N(s_N) \tag{6-4}$$

In this, the $u_i(\mathbf{r}_i)$ are one-electron orbital functions. The $\chi_i(s_i)$ are either $\alpha(s_i)$ or $\beta(s_i)$, the conventional spin function α referring to $m_s = +\frac{1}{2}$ and β to $m_s = -\frac{1}{2}$. Such a simple product function is the simplest conceivable function expressing the idea that the state is characterized by a configuration specified by the one-electron u_i functions. Clearly such a function is only approximate because, for one thing, it completely omits all *correlation* of the coordinates of the electrons; i.e., the probability distribution of r_1 is independent of where $r_2 \cdots r_N$ might be at the time. In fact, the e^2/r_{ij} Coulomb repulsion will tend to keep the electrons away from each other in the true wavefunction. Since no allowance is made for that here, the energy of the Hartree function must exceed the correct (and minimum) energy. However, within the framework of all functions which can be written as simple products, there should be a "best" one characterized by a set of functions $u_1 \cdots u_N$ which together give the lowest energy. These best functions are the so-called "Hartree functions," which have been calculated numerically for many atoms. Since the entire functional form is adjustable, better results should be possible than with a restricted analytic approximation to $u_i(r)$.

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[1] E. A. Hylleraas, *Z. Physik*, **54**, 347 (1929).

[2] T. Kinoshita, *Phys. Rev.*, **105**, 1490 (1957).

[3] C. L. Pekeris, *Phys. Rev.*, **112**, 1649 (1958).

These functions are found by iteration. First one guesses a set of functions $u_1 \cdots u_N$. Then one calculates the spherically averaged potential U_i seen by each electron by averaging the potential produced by the *other* electrons ($j \neq i$) and the nucleus.

$$U_i(r_i) = \frac{-Ze^2}{r_i} + \left[\sum_{j\neq i}\frac{e^2}{r_{ij}}\right]_{\text{av.}} \tag{6-5a}$$

The Schrodinger equation containing these potentials,

$$\left[\frac{\mathbf{p}_i^2}{2m} + U_i(r_i)\right]u_i = E_i u_i \tag{6-5b}$$

is solved by numerical integration. The resulting set of u_i will not in general agree with the assumed one. On the basis of this new set, another guess is made, and the calculation is repeated over and over until *self-consistency* is reached. One can show that these self-consistent solutions to the set of coupled integrodifferential equations described above (the "Hartree equations") also satisfy the variational requirement of lowest energy. The self-consistent potential $U_i(r_i)$ for the valence electrons is the proper potential to use in calculating the spin-orbit interaction function $\xi(r)$ if it is desired to calculate multiplet splittings. The Hartree functions for a large number of atoms have been calculated and tabulated by various authors. A review of the method, together with an index to the early calculations, has been given by Hartree.[1] Another listing is given in the Landolt-Bornstein tables (1951 edition), and Slater[2] has given a bibliography of calculations up to 1958. These indices also include reference to the more accurate Hartree-Fock functions, which we consider next.

Antisymmetric functions. Although the Hartree functions are good, they suffer from a serious group-theoretical objection. All electrons are identical or dynamically equivalent. Therefore $u_2(1)u_1(2)$ must be just as good a wavefunction as $u_1(1)u_2(2)$, and it must have the same energy. Thus any linear combination would serve. In general we might expect that we could replace the simple product function by

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[1] D. R. Hartree, *Repts. Progr. Phys.*, **11**, 113 (1946–1947). See also Hartree's book, "The Calculation of Atomic Structures," J. Wiley & Sons, Inc., New York, 1957, which lists work up to 1956.

[2] J. C. Slater, "Quantum Theory of Atomic Structure," vol. I, app. 16, McGraw-Hill Book Company, Inc., New York, 1960.

$$\psi = \sum_p c_p P[u_1(1)u_2(2)\cdots u_N(N)]$$

where P permutes the order of the electrons and c_p gives the weighting of the Pth permutation.

Because the electrons are in fact identical, no physically observable quantity (matrix element) can depend on the numbering. That is,

$$\bar{f} = \int \psi^*(1\cdots N) f \psi(1\cdots N)\, d\tau_1 \cdots d\tau_N$$

must be unchanged for an arbitrary exchange of r_i and r_k for an arbitrary function f. This is possible only if $P_{ik}\psi = e^{i\delta}\psi$, so that $(P_{ik}\psi)^*(P_{ik}\psi) = \psi^*\psi$. There is a further restriction imposed by the fact that $P_{ik}^2\psi = \psi$, which must be true since the second interchange simply restores the original order. These two requirements may be satisfied only if we have

$$P_{ik}\psi = (\pm 1)\psi \tag{6-6}$$

That is, the wave function is allowed to belong only to these two one-dimensional representations of the permutation group—the *symmetric* and the *antisymmetric*. Experimental evidence (Pauli exclusion principle, etc.) shows that electrons, protons, and all other half-integral spin particles (fermions) belong to the antisymmetric representation; on the other hand, all particles with integral spin (bosons) belong to the symmetric representation.

From the above discussion it follows that any correct electronic eigenfunction must be antisymmetric under interchange of electrons. The simple Hartree functions lack this property. However, we can antisymmetrize them or any other functions with the antisymmetrizing operator A. This operator is defined by

$$\Psi = A\psi = (N!)^{-\frac{1}{2}} \sum_P (-1)^p P\psi(r_1, \ldots, r_N) \tag{6-7}$$

where p is the number of binary permutations in the permutation P. This function Ψ has the required antisymmetric property, since interchanging i, j changes all the p's by 1, thus changing the sign of $A\psi$. The factor $(N!)^{-\frac{1}{2}}$ preserves normalization if ψ is a product of orthonormal u_i's. Note that, applied to such a product, this operator is equivalent to forming the determinant

$$\Psi = (N!)^{-\frac{1}{2}} \begin{vmatrix} u_1(1) & u_2(1) & \cdots & u_N(1) \\ u_1(2) & u_2(2) & \cdots & u_N(2) \\ \cdots & \cdots & \cdots & \cdots \\ u_1(N) & \cdots & \cdots & u_N(N) \end{vmatrix} \tag{6-8}$$

[The notation $u_1(1)$ now includes both space and spin parts.] These "Sla determinants" are the simplest generalization of the simple product fu tion to have the proper symmetry under permutation of identical particl Accordingly, they play a leading role in quantum mechanical calculations.

We can draw two simple but important inferences directly from th determinantal form of electronic wavefunctions:

1. If $u_i = u_j$, two columns are identical and the determinant vanish This gives us the elementary form of the *Pauli principle* forbidding mo than one electron in any given eigenstate.

2. If $(r_i, s_i) = (r_i, s_j)$, there are two identical rows and again the deter minant vanishes. This shows that two electrons with parallel spins ar never at the same place in real space and, by continuity, seldom very near t each other. This fact introduces a *kinematic correlation* of electrons with *parallel spin* which reduces the Coulomb-repulsion energy. Since this energ lowering is a consequence of the antisymmetry which is required by th "exchange degeneracy," this physical correlation turns out to be the basi for the intra-atomic "exchange energy" which causes parallel spins (maximum value of S) to lower the energy as stated in the first *Hund rule*.

Hartree-Fock functions. If we now seek the best functions which can be written as a single determinant of this sort, the variational method again leads to a set of coupled integrodifferential equations for the single-electron functions u_i. These more complicated equations are called the *Hartree-Fock equations*, and they were first found independently by Fock and by Slater in putting Hartree's rather intuitive method on a sounder mathematical footing. These equations are also solved numerically by iteration to self-consistency. In recent years, Hartree-Fock functions have usually been calculated rather than the simpler Hartree functions, though the results are not radically different. They *are* better, however, and have the practical advantage that the various u_i are rigorously orthogonal to each other. This was not true for the Hartree functions, since in that case a different potential is used for each subshell of the atom. Actually, the Hartree-Fock functions also have a different effective potential for each u_i. However, it turns out that the exchange terms introduced by the antisymmetry assure orthogonality. We defer our derivation and discussion of the Hartree-Fock equations until after the next section, in which we develop the tools needed for all calculations with determinantal wavefunctions.

6-4 Calculation of Matrix Elements between Determinantal Wavefunctions

We shall require many matrix elements of various operators between determinants of orthonormal functions. All those of most interest are either one- or two-electron operators. This allows us to reduce the whole procedure to a few rules, which we now derive.

Matrix elements of $F = \sum_i f(r_i)$. The simplest type of operator is a sum of identical one-electron operators, each operating on the coordinates of one electron. Examples are $T = (-\hbar^2/2m)\sum_i \nabla_i^2$, $V_Z = -\sum_i Ze^2/r_i$, and $\boldsymbol{\mu} = e\sum_i \mathbf{r}_i$. We are interested in the matrix element

$$(A\,|F|\,B) = \int \cdots \int \Psi^*(A) F \Psi(B)\, d\tau_1 \cdots d\tau_N \tag{6-9}$$

where $\Psi(A)$ is the antisymmetrized product (sometimes abbreviated AP)

$$\Psi(A) = (N!)^{-\frac{1}{2}} \sum_P (-1)^p P\psi(A) = \mathcal{A}\{a_1(1)a_2(2)\cdots a_N(N)\} \tag{6-10}$$

We have now condensed our notation by writing a_i to mean the spin-orbital function characterized by the set of quantum numbers a_i. Expanding the matrix element yields

$$(A\,|F|\,B) = (N!)^{-1} \sum_i \sum_P \sum_{P'} (-1)^{p+p'} \int \cdots \int P\psi^*(A) f(i) P'\psi(B)\, d\tau_1 \cdots d\tau_N \tag{6-11}$$

We now choose to view the permutation operator P as operating on the quantum-number indices a_i rather than on the coordinates r_i, the two being quite equivalent. For example, if $P = P_{12}$,

$$\begin{aligned} P\psi(A) &= P[a_1(1)a_2(2)a_3(3)\cdots] \\ &= Pa_1(1)Pa_2(2)Pa_3(3)\cdots = a_2(1)a_1(2)a_3(3)\cdots \end{aligned}$$

Thus the integral above becomes

$$\int Pa_1(1)P'b_1(1)\, d\tau_1 \cdots \int Pa_i(i) f(i) P'b_i(i)\, d\tau_i \cdots \int Pa_N(N)P'b_N(N)\, d\tau_N$$

Each of these integral factors (except the ith) is an orthonormality integral which will vanish unless $Pa_k = P'b_k$, etc. Therefore at least $(N-1)$ of the set of N spin-orbital functions in A and in B must be the same. This gives us the selection rule

$$(A\,|F|\,B) = 0 \tag{6-12}$$

if A, B differ by more than one pair of occupied functions.

Now, let a_k and b_l be the two functions which differ in the two sets of functions A and B. The subscripts k, l will in general differ because to get consistent results we must establish a fixed ordering convention. Our convention for atoms is to order the nl values in the conventional order for specifying a configuration. Within a subshell, the order is in decreasi order of m_l values and, for each m_l, α before β in the spin functions. (O course, in molecular and solid-state problems, some other convenient convention is chosen.) We can then form a set B',

$$B' = a_1a_2 \cdots a_{k-1}b_la_{k+1} \cdots a_N$$

which will *not* in general be in conventional order, but in which all the functions are in the same position as in A. Now $\Psi(B') = \pm\Psi(B)$, the minus sign applying if B' differs from B by an odd number of interchanges. Then $(A\,|F|\,B) = \pm\,(A\,|F|\,B')$, the sign carrying through from the result of reordering.

We may calculate $(A\,|F|\,B')$ quite simply. In order that the product of orthonormality integrals shall not vanish, the permutations P and P' must be the same so as to keep corresponding functions together. Thus the $(-1)^{p+p'} = +1$, and all terms come in positively. Further, to get a nonzero contribution, P must be such as to bring the function a_k to the ith position. For a given i, there are $(N-1)!$ ways of doing this. But this can be done for each i; so the result must be multiplied by N. The $N(N-1)!/N!$ factors cancel, leaving

$$(A\,|F|\,B) = \pm \int a_k^*(1)f(1)b_l(1)\,d\tau = \pm(a_k\,|f|\,b_l) \qquad \blacktriangleright\ \text{(6-13)}$$

where the $\pm$ sign is determined by whether an even or odd permutation is required to bring b_l into register with a_k, starting in the standard order.

The argument is similar for the diagonal elements. However, since the two sets are now identical, no $\pm$ signs enter from rearrangements. P must always equal P'. Thus

$$(A\,|F|\,A) = (N!)^{-1} \sum_i \sum_P \int Pa_i^*(i)f(i)Pa_i(i)\,d\tau_i$$

For each of the N values of i, there are $(N-1)!$ ways of permuting the indices not equal to i when each of the N a_k's is moved into the ith position. Hence we obtain

$$(A\,|F|\,A) = \sum_{i=1}^{N} \int a_i^*(1)f(1)a_i(1)\,d\tau_1 = \sum_{i=1}^{N} (a_i\,|f|\,a_i) \qquad \blacktriangleright\ \text{(6-14)}$$

This result states the very reasonable conclusion that the expectation value of F in the many-electron state A is simply the sum of the expectation values of f over the occcupied orbitals a_i.

Matrix elements of $G = \sum_{i>j} g(i,j)$. Since we can assume that any terms of the sort $g(i,i)$ are handled by the rules just derived for functions of the type F, we lose no generality by excluding the diagonal terms in this two-electron operator G. Typical examples of operators of the type G are the Coulomb energy $\sum_{i>j} e^2/r_{ij}$ and the dipole-dipole energy $\sum_{i>j} r_{ij}^{-3}[\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j - 3(\mathbf{r}_{ij} \cdot \boldsymbol{\mu}_i)(\mathbf{r}_{ij} \cdot \boldsymbol{\mu}_j)/r_{ij}^2]$. For such operators, we have

$$(A\,|G\,|B) = (N!)^{-1} \sum_{i>j} \sum_{P'P} (-1)^{p+p'} \iint Pa_i^*(i)Pa_j^*(j)g(i,j)P'b_i(i)P'b_j(j) \times d\tau_i\, d\tau_j\, \delta(Pa_1, P'b_1) \cdots \delta(Pa_N, P'b_N) \qquad (6\text{-}15)$$

where the product of δ functions arises from the orthonormality integrals and omits a factor only for i and j. In this case, the selection rule is that

$$(A\,|G|\,B) = 0 \qquad (6\text{-}16)$$

if A, B differ by more than two pairs of functions. We then have to consider three possible cases: A, B differing by 2, 1, or 0 pairs of functions.

Considering first the case where A and B differ by two pairs of functions, we can rearrange B to B', as we did above, so that all the functions b_i which equal some a_i are paired off. This leaves the unmatched functions a_k and a_l paired off with the unmatched functions b_m and b_n. These can be paired either as $(k, l; m, n)$ or $(k, l; n, m)$, with the number of binary permutations, and hence the sign, changing from one to the other. By following a term-counting scheme like that given above for F, we then are led to the result

$$\begin{aligned}(A\,|G|\,B) &= \pm\left\{\iint a_k^*(1)a_l^*(2)g(1,2)b_m(1)b_n(2)\,d\tau_1\,d\tau_2 - \iint a_k^*(1)a_l^*(2)g(1,2)b_n(1)b_m(2)\,d\tau_1\,d\tau_2\right\} \\ &= \pm\{(a_ka_l\,|g|\,b_mb_n) - (a_ka_l\,|g|\,b_nb_m)\} \qquad \blacktriangleright\ (6\text{-}17)\end{aligned}$$

The $\pm$ sign is determined by the permutation required to bring B into B' with the pairing $(k, l;\ m, n)$.

By similar arguments, when A and B differ by only one pair $b_l \neq a_k$, we have

$$\begin{aligned}(A\,|G|\,B) &= \pm\sum_t\left\{\iint a_k^*(1)a_t^*(2)g(1,2)b_l(1)a_t(2)\,d\tau_1\,d\tau_2 - \iint a_k^*(1)a_t^*(2)g(1,2)a_t(1)b_l(2)\,d\tau_1\,d\tau_2\right\} \\ &= \pm\sum_t\{(a_ka_t\,|g|\,b_la_t) - (a_ka_t\,|g|\,a_tb_l)\} \qquad \blacktriangleright\ (6\text{-}18)\end{aligned}$$

where t runs over the $(N - 1)$ sets of functions common to A and B. Finally, the diagonal elements are given by

$$\begin{aligned}(A\,|G|\,A) &= \sum_{k>t=1}^{N}\left\{\iint a_k^*(1)a_t^*(2)g(1,2)a_k(1)a_t(2)\,d\tau_1\,d\tau_2 - \iint a_k^*(1)a_t^*(2)g(1,2)a_t(1)a_k(2)\,d\tau_1\,d\tau_2\right\} \\ &= \sum_{k>t}\{(a_ka_t\,|g|\,a_ka_t) - (a_ka_t\,|g|\,a_ta_k)\} \qquad \blacktriangleright\ (6\text{-}19)\end{aligned}$$

The integrals with positive sign are called *direct integrals* and the on with negative sign are called *exchange integrals* because the functions and a_k are exchanged between initial and final states in the integral. Th presence of the exchange integrals is strictly a consequence of our use of a antisymmetrized form. They would not occur, for example, if we evaluat $(A\,|G|\,A)$ using the simple product function $\psi(A)$. In general, all prop exchange terms arise from this antisymmetry.

If $g(i,j)$ is independent of spin, we can carry out the "integration" ov spin coordinates implied by the integral signs in a trivial manner. In th case of the off-diagonal elements, inspection of (6-17) and (6-18) show that $(A\,|G|\,B)$ will vanish between states differing in $M_S = \Sigma m_s$ because in each case m_s must match for each electron. This is as it must be, since if G is spin-independent, it must commute with S_z. In the diagonal element $(A|\,G|\,A)$, we get simply a factor of unity in the direct integral and a factor of $\delta(m_s{}^k, m_s{}^t)$ in the exchange integral. Thus there are exchange integrals of a spin-*independent* operator only for electrons of like spin. This introduces an energy which formally depends on the relative orientation of spins, and hence it plays a central role in magnetic problems, despite the fact that the fundamental interaction is usually the electrostatic energy e^2/r_{ij}, which has nothing magnetic about it. This term in the energy, proportional to $-\mathbf{s}_k \cdot \mathbf{s}_t$, is the formal basis for the Heisenberg–Dirac–Van Vleck[1] *vector model*, which has often been used in rather phenomenological treatments of magnetic problems. Stated more precisely, if we consider two electrons occupying two orthogonal orbitals a and b, one can readily show that the energies of singlet and triplet states are $E_0 + K_{12} \pm J_{12}$, where E_0 is the energy in the absence of any interaction between the electrons, $K_{12} = (ab\,|g|\,ab)$, and $J_{12} = (ab\,|g|\,ba)$. This can be written as $E_0 + K_{12} - \frac{1}{2}J_{12} - 2J_{12}\mathbf{s}_1 \cdot \mathbf{s}_2$. The spin-dependent part is then generalized to

$$-2 \sum_{k>l} J_{kl}\mathbf{s}_k \cdot \mathbf{s}_l \qquad (6\text{-}20)$$

Note that, if $J > 0$, spins tend to align parallel to give a lower energy. In fact, if $g(i,j) = e^2/r_{ij}$, the exchange integral can be proved to be positive definite.[2] This provides the quantum-mechanical basis for the Hund rule that the L-S term with maximum S has the lowest energy, and we see that it is based on electrostatic, not magnetic, interactions.

This result (6-20) also forms the basis of Heisenberg's theory of ferromagnetism of solids. However, since antiferromagnetic and diamagnetic materials are more common than ferromagnetic ones, it is clear that it must also be possible for J to be negative if (6-20) is to hold. As stated above, this is not possible with J defined as a proper exchange integral. If we combine all terms which depend on $\mathbf{s}_1 \cdot \mathbf{s}_2$, including those arising from nonorthogonality of the functions a, b as well as the proper exchange integral, either sign becomes possible. However, in this case J_{12} has become difficult to calculate, and in many cases it is really little more than a disposable parameter in a phenomenological treatment. Despite this fact, such treatments are often of great value in accounting for the behavior of physical systems in which *ab initio* calculations are much too difficult to be possible.[1] Further discussion of exchange integrals will be given in Sec. 7-6 on the Heitler-London Method.

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[1] J. H. Van Vleck, "Theory of Electric and Magnetic Susceptibilities," chap. 12, Oxford University Press, New York, 1932.

[2] J. C. Slater, "Quantum Theory of Atomic Structure," vol. I, app. 19, McGraw-Hill Book Company, Inc., New York, 1960.

6-5 Hartree-Fock Method

Our program is to use the variational theorem to find the best set of N one-electron orbitals to use in a determinantal wavefunction. This is done by minimizing the diagonal energy matrix element while constraining the functions to stay orthonormal. For definiteness, we take an atomic Hamiltonian, excluding small magnetic-energy terms like the spin-orbit coupling, namely,

$$H = \sum_i \left[\frac{\mathbf{p}_i^2}{2m} - \frac{Ze^2}{r_i}\right] + \sum_{i>j} \frac{e^2}{r_{ij}}$$

It should be emphasized, however, that the method is in principle equally applicable to molecular and solid-state problems if Ze^2/r is replaced by a suitably generalized many-center potential. We use the results of the last section, denoting the various orbitals (including spin) by u_i. This gives us

$$\int \Psi^* H \Psi \, d\tau = \sum_i \int u_i^*(1)\left[-\frac{\hbar^2 \nabla_1{}^2}{2m} - \frac{Ze^2}{r_1}\right] u_i(1)\, d\tau_1 + \sum_{i>j} \iint u_i^*(1) u_j^*(2) \left(\frac{e^2}{r_{12}}\right) \times u_i(1) u_j(2)\, d\tau_1\, d\tau_2 - \sum_{i>j,\parallel} \iint u_i^*(1) u_j^*(2) \left(\frac{e^2}{r_{12}}\right) u_j(1) u_i(2)\, d\tau_1\, d\tau_2 \tag{6-21}$$

The last sum is to be taken only over pairs of electrons with parallel spins, because they are the exchange integrals and e^2/r_{12} is independent of spin. Now we imagine one of the $u_i(r)$ to be varied by a small amount $\delta u_i(r)$; this of course produces a like change δu_i^* in u_i^*. One can show that all terms arising from the variation of u_i^* are complex conjugates of those arising from the variation in u_i. This is elementary for the potential-energy terms but requires an application of Green's theorem for the term in ∇^2. Thus, if we make the energy insensitive in first order to change in u_i^* alone, we have already satisfied our requirement for an extremal energy. Since we also wish to preserve the normalization of the u_i, we add the Lagrange multiplier $(-\epsilon_{ii})$ times the normalization integral $\int u_i^*(1)u_i(1)\,d\tau_1$ to our energy integral before performing the variation. Further, to preserve orthogonalization, we add the orthogonality integrals $\int u_i^*(1)u_j(1)\,d\tau_1$ with Lagrange multipliers $-\epsilon_{ij}$. By the usual method in the calculus of variations, we then argue that, if the sum of integrals is to vanish for an arbitrary δu_i^*, the coefficient of δu_i^* must be everywhere zero. This leads directly to the Hartree-Fock equation,

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[1] It is perhaps symbolic of the gulf between these two approaches that in the *ab initio* literature J and K are commonly used for the direct and exchange integrals, respectively, whereas in the "vector-model" literature, the usage is usually the reverse.

$$\left[-\frac{\hbar^2\nabla_1^2}{2m}-\frac{Ze^2}{r_1}\right]u_i(1)+\sum_{j\neq i}\left[\int u_j^*(2)\left(\frac{e^2}{r_{12}}\right)u_j(2)\,d\tau_2\right]u_i(1)$$
$$-\sum_{j\neq i,\parallel}\left[\int u_j^*(2)\left(\frac{e^2}{r_{12}}\right)u_i(2)\,d\tau_2\right]u_j(1)=\sum_j \epsilon_{ij}u_j(1) \qquad \blacktriangleright\ (6\text{-}22)$$

The terms in the first line are exactly those which we had in the simple Hartree case: the kinetic energy, the potential energy due to the nucleus, and the Coulomb repulsion averaged over the positions of the other electrons. The exchange integrals do not appear in the Hartree equations because they arise only with antisymmetrized functions. Also, since the Hartree functions are not orthogonal, we have no terms in the right member except $\epsilon_{ii}u_i(1)$, because the other Lagrange multipliers would not appear. In this way, we see how the Hartree equations (6-5) follow from a variational approach if we neglect antisymmetry.

Let us now clarify these extra terms which distinguish the Hartree-Fock from the Hartree equations. First, we note that only the best *determinant* is fixed by the variational principle. Since a determinant is unchanged by a unitary transformation, the u_i are *not* completely determined. This freedom can be used to throw ϵ_{ij} into diagonal form, so that we again have only the single term $\epsilon_{ii}u_i = E_iu_i$ appearing in Eq. (6-22). We shall assume that this simplification has in fact been carried through.

To give more physical insight into the remaining sum of exchange integrals which arises from the antisymmetry, we follow a method suggested by Slater.[1] First, he observes that we can remove the restriction that $j \neq i$ in both the summations, since the two integrals added in this way just cancel each other. Then, if we multiply and divide the exchange term by $u_i^*(1)u_i(1)$, we have the following revised form of the Hartree-Fock equations:

$$\left[-\frac{\hbar^2\nabla_1^2}{2m}-\frac{Ze^2}{r_1}\right]u_i(1)+\left[\sum_j\int u_j^*(2)\left(\frac{e^2}{r_{12}}\right)u_j(2)\,d\tau_2\right]u_i(1)$$
$$-\left[\sum_{j\parallel i}\frac{\int u_i^*(1)u_j^*(2)(e^2/r_{12})u_j(1)u_i(2)\,d\tau_2}{u_i^*(1)u_i(1)}\right]u_i(1)=E_iu_i(1) \qquad (6\text{-}23)$$

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[1] J. C. Slater, *Phys. Rev.*, **81**, 385 (1951).

This now looks exactly like $Hu_i = E_iu_i$. The effective Hamiltonian now includes the kinetic energy, nuclear attraction, the repulsion of *all* electrons (including the one we are interested in), and the last term. Since we can be sure the electron really exerts no force on itself, this last term must somehow take care of that fact. The last term is negative and subtracts the repulsion of a charge density at $\mathbf{r}_2$ of magnitude (apart from a factor e)

$$\rho_{\text{ex}}{}^{(i)}(1, 2) = \sum_{j \| i} \frac{u_i^*(1)u_j^*(2)u_j(1)u_i(2)}{u_i^*(1)u_i(1)} \tag{6-24}$$

We call this the *exchange charge density* seen by the electron in the ith function when it is at $\mathbf{r}_1$. Integration over $\mathbf{r}_2$, upon using the orthogonality of u_i and u_j for $i \neq j$, shows that this exchange charge density contains exactly one electron. Further, at $\mathbf{r}_2 = \mathbf{r}_1$, $\rho_{\text{ex}}{}^{(i)}(1, 1) = \sum_{j \| i} |u_j(1)|^2$. That is, it exactly subtracts out the charge density of all electrons with spin parallel to that of the ith function at $\mathbf{r}_1$. This is consistent with our earlier remark that the antisymmetry guaranteed that electrons with parallel spin were never at the same point in space. The exact shape of $\rho_{\text{ex}}(1, 2)$ will depend on the details of the u's. However, to a crude approximation, it will have the effect of removing all the parallel spin charge from a sphere centered at $\mathbf{r}_1$ and of radius R such that

$$\int \rho_{\text{ex}}\, d\tau \approx \frac{4\pi}{3} \sum_{j \| i} |u_j(1)|^2 R^3 = 1 \tag{6-25}$$

More pictorially, each electron moves in the field of the nucleus, the electrons of opposite spin, and those of parallel spin outside an "exchange hole," or "Fermi hole" (of radius R), which follows around wherever it goes.

Slater has used this physical picture as the basis for a simplified form of the Hartree-Fock equations. In this he forms a suitable *average* exchange charge density for electrons of each spin and then calculates *all* his eigenfunctions in the resulting two potentials, which are, of course, identical if there are no unpaired spins in the system. This eliminates the complications which arise from having each electron move in a different potential. The approximation is particularly useful in handling excited states, for excited orbitals can be calculated which are automatically orthogonal to the normal ones because they arise from the same Hamiltonian.

It should be noted that the effective Hartree-Fock potential *does* depend on the spin orientation, unless the atom has only paired spins throughout. This has important consequences for the wave functions in magnetic atoms. In particular, it produces a difference in the orbital functions associated with up and down spins, even for inner shells where both are occupied. To treat this accurately, one must resort to the *unrestricted Hartree-Fock method*,[1] in which the usual simplifying restriction that the orbital functions depend only on n, l, m_l (not m_s) is dropped. This doubles the number functions to be determined and hence is not ordinarily used except in treat effects depending directly on the *difference* between the up- and down-s functions.

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[1] G. W. Pratt, Jr., *Phys. Rev.*, **102**, 1303 (1956).

An important example of such an effect is in the hyperfine struct coupling in Mn^{++}. This ion has a nominal $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ configurati Since all the inner subshells are complete, the magnetic properties of the i arise from the five d electrons whose spins are parallel in accordance wi the Hund rule. As we shall see in Sec. 6-11, the dominant hyperfi coupling term is proportional to the density of unpaired spins at the nucle Since a d function must vanish as r^2 as $r \to 0$, there is no direct coupling the $3d$ electrons and there would be no "contact" hyperfine splitting in t restricted Hartree-Fock approximation. Actually, a very sizable splitti is observed. This has been computed with fair success by Wood and Pra and by Heine[2] by use of the unrestricted Hartree-Fock method with t Slater approximation for the exchange potential. They find that the $1s$ a $2s$ orbitals for spins parallel to the $3d$ spins are pulled outward by the a tractive exchange potential, leaving a negative net spin density at the nucle The effect on the $3s$ orbitals, which are peaked at about the same radius the $3d$, is of opposite sign but less in magnitude. The resultant effect is the correct sign and order of magnitude (about 1 per cent unbalance betwe spin densities), whereas previous calculations[3] using an apparently more r stricted approach had yielded a result which was an order of magnitu too small.

6-6 Calculation of *L-S*-term Energies

Degeneracy within a configuration. If the configuration consists entire of closed shells, there is only one possible determinantal eigenfunction. F example, if we have six p electrons, the wavefunction must be

$$\Psi = A\{p_1\alpha(1)p_1\beta(2)p_0\alpha(3)p_0\beta(4)p_{-1}\alpha(5)p_{-1}\beta(6)\} \tag{6-25a}$$

where A is our antisymmetrizing operator defined in (6-7). We shall ofte condense this notation still further to write

$$\Psi = (1^+\,1^-\,0^+\,0^-\,-1^+\,-1^-) \tag{6-25b}$$

No other assignment of six p electrons would be consistent with the e clusion principle.

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[1] J. H. Wood and G. W. Pratt, *Phys. Rev.*, **107,** 995 (1957).

[2] V. Heine, *Phys. Rev.*, **107,** 1002 (1957).

[3] A. Abragam, J. Horowitz, and M. H. L. Pryce, *Proc. Roy. Soc.* (*London*), **A230,** 16 (1955).

If a shell is not full, we have many possibilities—all belonging to the same configuration. For example, if we have two inequivalent p electrons, such as $2p3p$, 36 possible determinants can be formed, since each electron has its choice of six states. Even if we consider two *equivalent p* electrons, we have $\binom{6}{2} = 15$ possible determinants. All these determinants must have the same energy in the purely central-field approximation. Therefore, when we introduce the interelectronic perturbation

$$H' = \sum_{i>j} \frac{e^2}{r_{ij}} - \sum_i \left[U(r_i) + \frac{Ze^2}{r_i} \right]$$

we must solve the secular equation

$$|(H^0 + H')_{ij} - E\delta_{ij}| = 0 \qquad (6\text{-}27)$$

connecting these states exactly—that is, without any perturbation-theory approximation—because all the diagonal elements $H_{ii}{}^0$ are the same. Obviously this would involve an immense amount of labor if no means were available to help factor the secular equation. Fortunately, the group-theoretical properties of angular-momentum operators provide a large amount of initial factorization.

Factorization by angular momentum. The method is based on the fact that the approximate Hamiltonian H is invariant, not only under an overall rotation of coordinates, but also under separate rotation of spatial and spin coordinates, so long as we are neglecting spin-orbit coupling. In other words, H commutes, not only with $\mathbf{J}$, but also with $\mathbf{L}$ and $\mathbf{S}$. We may then apply our matrix-element theorem (Sec. 4-9 or 5-11) for invariant (scalar) operators to state that there can be no matrix elements of H between states with different L, S, or J or different M_L, M_S, or M_J, since these quantum numbers label the irreducible representations and their rows. Thus we can factor the secular equation by choosing determinants, or linear combinations of determinants, which are already angular-momentum eigenfunctions.

We are limited in the extent we can go in this direction by the fact that all angular momenta that commute with H do not commute with each other. We can simultaneously diagonalize four angular-momentum operators. The most useful sets have the good quantum numbers

$$LSM_LM_S \qquad \text{and} \qquad LSJM$$

It is easiest to start with the LSM_LM_S sets, since we are using one-electron functions characterized by m_l and m_s. Thus we automatically give "sharp" values to $M_L = \Sigma m_l$ and $M_S = \Sigma m_s$. Then, if we sort out states by their M_L and M_S values, we shall already have achieved a great amount of factorization. As an example, we consider our np^2 example of two equivalent p electrons. We may then classify all the 15 determinants consistent with the exclusion principle as in Table 6-1. Evidently only the upper left quadrant of this table need be written out, since the others can be obtained by suitable systematic sign changes. Since there are no matrix elements between states of different M_L or M_S, inspection of this table shows that our 15×15 secular equation will factor down to eight 1×1's, two 2×2's, and one 3×3, by $M_L M_S$ factorization alone.

Table 6-1

Possible np^2 determinants

		M_S	
M_L	1	0	-1
2		(1^+1^-)	
1	(1^+0^+)	$(1^+0^-)(1^-0^+)$	(1^-0^-)
0	$(1^+\ -1^+)$	$(1^+\ -1^-)(1^-\ -1^+)(0^+0^-)$	$(1^-\ -1^-)$
-1	$(0^+\ -1^+)$	$(0^+\ -1^-)(0^-\ -1^+)$	$(0^-\ -1^-)$
-2		$(-1^+\ -1^-)$	

To proceed further, we must inquire after the L and S values as well. For example, the state (1^+1^-) must have $L \geqq 2$, since $M_L = 2$. But in combining two systems with $l = 1$, the vector model allows only $L = 0$, 1, 2; therefore, it must be a D state ($L = 2$). Since only one state with $M_L = 2$ exists, it must be part of a ${}^1D$ term, since for ${}^3D$ we would have to have two others with $M_S = \pm 1$. These are forbidden by the exclusion principle, however, since they would require double occupancies like (1^+1^+). Now that we know that a ${}^1D$ term is present, we must also have the other four "partners" in the five-dimensional representation. This accounts for 1 state out of each row of the $M_S = 0$ column. The remaining 10 states are easily seen to be those required for a ${}^3P(M_L = \pm 1, 0;\ M_S = \pm 1, 0)$ and a ${}^1S\ (M_L = M_S = 0)$ term. It is in this way that we obtain the result that the terms allowed by the Pauli principle in the np^2 configuration are ${}^1D$, ${}^3P$, and ${}^1S$.

At this time we might note that only for the cases in Table 6-1 where there is only one determinant are these determinants also eigenfunctions of L and S. In the other cases, each determinant is a mixture of the various L-S terms represented therein. It is easily possible to find the linear combinations within a set which also diagonalize L and S. For example, by using

$$L_-\Psi(L = 2, M_L = 2, S = 0) = L_-(1^+1^-)$$

$$= \sqrt{L(L+1) - 2 \cdot 1}\,\Psi(L = 2, M_L = 1, S = 0)$$

and the methods developed in Sec. 6-8, we find that

$$\psi(L = 2, M_L = 1, S = 0) = \frac{[(1^+0^-) - (1^-0^+)]}{\sqrt{2}}$$

In this way, we could find linear combinations of determinants which would completely diagonalize the Hamiltonian in this example. However, another method, due to Slater, is still more efficient in obtaining the energy eigenvalues which we seek.

Slater sum-rule method. This method is based on the fact that the energy of an L-S term is independent of M_L and M_S. Thus we have only three *distinct* eigenvalues to find from our 15 × 15 problem, namely, the energies of the ${}^1D$, ${}^3P$, and ${}^1S$ terms. We can calculate these energies for whatever M_L and M_S are most convenient. When possible we choose M_L and M_S so that there is only one determinant in the set, assuring us that we are dealing with an eigenfunction of L and S, that is, a pure term. For example,

$$E({}^1D) = (1^+1^- |H| 1^+1^-)$$

and

$$E({}^3P) = (1^+0^+ |H| 1^+0^+) \tag{6-28a}$$

All that remains to find is $E({}^1S)$. This will be one of the three roots of the 3 × 3 secular equation obtained from the three determinants with $M_L = M_S = 0$. But we already know the other two roots, $E({}^1D)$ and $E({}^3P)$, and by the invariance of traces under unitary transformations, we know that the sum of the three roots is just the sum of the three diagonal energies. Thus we can express our unknown energy somewhat symbolically as

$$\begin{aligned} E({}^1S) &= Tr\,(3 \times 3) - E({}^1D) - E({}^3P) \\ &= \langle 1^+ -1^- \rangle + \langle 1^- -1^+ \rangle + \langle 0^+0^- \rangle - \langle 1^+1^- \rangle - \langle 1^+0^+ \rangle \end{aligned} \tag{6-28b}$$

where in the last line we have abbreviated the notation for diagonal matrix elements still further.

Thus we have succeeded in finding all the distinct eigenvalues of a 15 × 15 secular equation by calculating only five diagonal matrix elements. This trick is of very general utility and handles all cases until we have two distinct terms with the same L-S values arising from the same configuration. In this case, one must actually solve a small secular equation, because rotational symmetry is no longer enough to determine the eigenfunctions completely.

6-7 Evaluation of Matrix Elements of the Energy

Let us examine these diagonal matrix elements to which we have reduced the problem. They are matrix elements of

$$H = \sum_i \left[\frac{\mathbf{p}_i^2}{2m} - \frac{Ze^2}{r_i}\right] + \sum_{i>j} \frac{e^2}{r_{ij}}$$

Now, the one-electron terms will contribute equally to all diagonal elements since all come from the same configuration. Thus these terms only shift the energetic center of gravity for the configuration and have no effect on the splitting apart of the terms. This term structure is determined wholly by $Q = \sum_{i>j} e^2/r_{ij}$.

Applying our general results for operators of the type G, we have

$$(A\,|Q|\,A) = \sum_{a>b}\left[\left(ab\left|\frac{e^2}{r_{12}}\right|ab\right) - \left(ab\left|\frac{e^2}{r_{12}}\right|ba\right)\right] \tag{6-29}$$

This sum runs over all pairs of electrons and may be broken up into three parts: (1) pairs in closed shells, (2) pairs with one electron in a closed shell, and (3) pairs with neither electron in a closed shell. Since closed shells have spherical symmetry (Unsold's theorem), we do not expect terms like (1) and (2) to split the terms when summed over all occupied states. Rather, they represent the "shielding" effect of the inner closed shells upon the potential experienced by the valence electrons. This fact may be proved rigorously[1], but since it seems physically evident as well, we shall omit the formal proof here. This leaves the entire splitting to be determined by the part

$$(A\,|Q|\,A) = \sum_{a>b=1}^{N'} [J(a, b) - K(a, b)] \tag{6-30}$$

where N' includes only the electrons not in closed shells and J and K are the conventional symbols for the direct and exchange integrals of the Coulomb interaction. This substantiates our earlier statement that the energy differences among the L-S terms belonging to a given configuration arise from the Coulomb repulsion.

Calculation of matrix elements of the electrostatic interaction. Rather than calculate simply the diagonal elements required in using the Slater sum rule, we shall set up the machinery for handling the most general case that can arise. This has the form

$$(ab\,|q|\,cd) = \iint a^*(1)b^*(2)\left(\frac{e^2}{r_{12}}\right)c(1)d(2)\,d\tau_1\,d\tau_2 \tag{6-31}$$

where typically

$$a(1) = \left(\frac{1}{r_1}\right)R_{n^al^a}(r_1)\Theta_{l^am_l{}^a}(\theta_1)\Phi_{m_l{}^a}(\varphi_1)\chi_{m_s{}^a}(s_1) \tag{6-32a}$$

For ease in writing, we shall write this

$$a(1) = \left(\frac{1}{r_1}\right)R_1(n^al^a)\Theta_1(l^am_l{}^a)\Phi_1(m_l{}^a)\chi_1(m_s{}^a) \tag{6-32b}$$

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[1] Condon and Shortley, *op. cit.*, p. 182.

The integral is then a sixfold integral over spatial coordinates and a twofold summation over spin coordinates. The spin sum gives zero unless $m_s^a = m_s^c$ and $m_s^b = m_s^d$. If these hold, the sum yields unity, and we have only the spatial integrals to deal with.

To proceed, we expand $1/r_{12}$ in the conventional way,

$$\frac{1}{r_{12}} = \frac{1}{(r_1^2 + r_2^2 - 2r_1r_2 \cos \omega)^{\frac{1}{2}}} = \sum_{k=0}^{\infty} \frac{r_<^{\,k}}{r_>^{\,k+1}} P_k (\cos \omega) \tag{6-33}$$

where $r_<$ and $r_>$ are the lesser and greater of $|r_1|$, $|r_2|$ and ω is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$. Next, we expand $P_k (\cos \omega)$, using the spherical harmonic addition formula,

$$P_k(\cos \omega) = \frac{4\pi}{2k + 1} \sum_{m=-k}^{k} \Theta_1(km)\Theta_2(km)\Phi_1(m)\Phi_2^*(m) \tag{6-34a}$$

where
$$\cos \omega = \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos (\varphi_1 - \varphi_2) \tag{6-34b}$$

Integrating the resulting expression over φ_1 and φ_2 merely gives δ functions which assure conservation of L_z (together with a normalization factor of $\left.\frac{1}{2\pi}\right)$. Thus the matrix element vanishes unless

$$m = m_l^a - m_l^c = m_l^d - m_l^b$$

or
$$m_l^a + m_l^b = m_l^c + m_l^d$$

This is as it must be, since e^2/r_{12} is invariant under a general rotation of coordinates of *all* particles. The remaining integral is

$$\begin{aligned}(ab\,|q|\,cd) = 2e^2 \sum_{k=0}^{\infty} \frac{1}{2k + 1} \int_0^{\infty} \int \frac{r_<^{\,k}}{r_>^{\,k+1}} R_1(n^a l^a)R_2(n^b l^b)R_1(n^c l^c)R_2(n^d l^d)\, dr_1\, dr_2 \\ \times \int_0^{\pi} \int \Theta_1(l^a m_l^a)\Theta_2(l^b m_l^b)\Theta_1(l^c m_l^c)\Theta_2(l^d m_l^d) \\ \times \Theta_1(k, m_a - m_c)\Theta_2(k, m_l^d - m_l^b) \sin \theta_1 \sin \theta_2\, d\theta_1\, d\theta_2\end{aligned} \tag{6-35}$$

or

$$\begin{aligned}(ab\,|q|\,cd) = \delta(m_s^a, m_s^c)\delta(m_s^b, m_s^d)\delta(m_l^a + m_l^b, m_l^c + m_l^d) \sum_{k=0}^{\infty} c_k(l^a m_l^a, l^c m_l^c) \\ \times c^k(l^d m_l^d, l^b m_l^b) R^k(n^a l^a n^b l^b, n^c l^c n^d l^d)\end{aligned} \tag{▶ 6-36}$$

The coefficients c^k are integrals of products of three Legendre functions. These have been worked out by Gaunt and tabulated once and for all.[1] The formal definition is

$$c^k(lm_l, l'm_l') = \sqrt{\frac{2}{2k + 1}} \int_0^{\pi} \Theta(k, m_l - m_l')\Theta(lm_l)\Theta(l'm_l') \sin \theta\, d\theta \tag{6-37}$$

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[1] J. A. Gaunt, *Trans. Roy. Soc. (London)*, **A228**, 195 (1928). A more accessible table of results may be found in Condon and Shortley, *op. cit.*, pp. 178–179; a table adequate for *s*, *p*, *d* electrons is given in Appendix C of this book.

We note that $c^k(lm_l, l'm_l') = (-1)^{m_l - m_l'} c^k(l'm_l', lm_l)$ follows from our sta ard phase choice for the $\Theta(lm_l)$. Actually these Gaunt coefficients c^k c be readily expressed in terms of Wigner coefficients, and in fact this ent development could be carried out within the framework of the tens operator formalism which we developed in the previous chapter. We sh not do this here, however, but shall simply state that the connection

$$c^k(lm_l, l'm_l') = \left[\frac{(2l'+1)}{(2l+1)}\right]^{\frac{1}{2}} A^{kl'l}_{000} A^{kl'l}_{m_l - m_l', m_l', m_l} \tag{6-37}$$

where the $A^{j_1j_2j_3}_{m_1m_2m_3}$ are the Wigner coefficients. The other quantity, R^k, i radial integral which depends on the particular approximate form for t radial wave function. The definition is just

$$R^k(n^al^an^bl^b, n^cl^cn^dl^d) = e^2 \int_0^\infty \int \frac{r_<^{\ k}}{r_>^{\ k+1}} R_1(n^al^a)R_2(n^bl^b)R_1(n^cl^c)R_2(n^dl^d)\, dr_1\, dr \tag{6-3}$$

These radial integrals may have to be evaluated numerically if we use H tree functions, for example. Luckily, in most cases of interest, only a f terms in the sum on k in (6-36) are nonzero, because of the properties the c^k. That is, $c^k(l, l') = 0$ unless k satisfies the vector-model conditio $|l - l'| \leqslant k \leqslant l + l'$ and unless further $k + l + l' =$ even. This limitatio on the number of k values allows these remaining integrals R^k to be used parameters in describing the term structure, and interesting results for *rat* of term separations may often be deduced by using only the c^k, which a tabulated.

Diagonal elements. Since only the diagonal elements are needed for usi the Slater method, we now specialize our results for this case. We ha

$$(A\,|Q|\,A) = \sum_{a>b} [J(a, b) - K(a, b)] \equiv \sum_{a>b} [(ab\,|q|\,ab) - (ab\,|q|\,ba)]$$

Because of the symmetry which exists when only two distinct orbitals $(a,$ are involved, we can condense the notation and reduce our general e pression to

$$J(a, b) = \sum_{k=0}^{\infty} a^k(l^am_l^{\ a}, l^bm_l^{\ b})F^k(n^al^a, n^bl^b) \tag{6-39}$$

and

$$K(a, b) = \delta(m_s^{\ a}, m_s^{\ b}) \sum_{k=0}^{\infty} b^k(l^am_l^{\ a}, l^bm_l^{\ b})G^k(n^al^a, n^bl^b) \tag{6-39}$$

where we have introduced the new notations

$$a^k(l^am_l^{\ a}, l^bm_l^{\ b}) = c^k(l^am_l^{\ a}, l^am_l^{\ a})c^k(l^bm_l^{\ b}, l^bm_l^{\ b}) \tag{6-40}$$

$$b^k(l^am_l^{\ a}, l^bm_l^{\ b}) = [c^k(l^am_l^{\ a}, l^bm_l^{\ b})]^2 \tag{6-40}$$

and

$$F^k(n^al^a, n^bl^b) = R^k(n^al^an^bl^b, n^al^an^bl^b) \tag{6-41}$$

$$G^k(n^al^a, n^bl^b) = R^k(n^al^an^bl^b, n^bl^bn^al^a) \tag{6-41}$$

These coefficients a^k and b^k have also been tabulated.[1] We note that $F^k = G^k$ if the electrons are equivalent.

Example (np^2). As shown in (6-28), in order to get the L-S-term energies, we need the diagonal energies $\langle 1^+1^- \rangle$, $\langle 1^+0^+ \rangle$, $\langle 1^+ -1^- \rangle$, $\langle 1^- -1^+ \rangle$, and $\langle 0^+0^- \rangle$. Apart from the common additive constant coming from the closed shells,

$$\begin{aligned}\langle 1^+1^- \rangle &= J(1^+1^-) - K(1^+1^-)\\ &= \sum_k a^k(p, 1, p, 1)F^k(np, np) - 0\end{aligned}$$

Inspecting the tables of a^k coefficients, we find that the only nonvanishing coefficients are for $k = 0, 2$. Thus

$$\langle 1^+1^- \rangle = F^0(np, np) + (\tfrac{1}{25})F^2(np, np) = F_0(np, np) + F_2(np, np)$$

where we have indicated the absorption of numerical constants into the F^k by dropping the superscript to a subscript. Similarly,

$$\begin{aligned}\langle 1^+0^+ \rangle &= J(1^+0^+) - K(1^+0^+)\\ &= \sum a^k(p, 1, p, 0)F^k(np, np) - \sum b^k(p, 1, p, 0)G^k(np, np)\\ &= F^0 - \frac{2F^2}{25} - \frac{3F^2}{25}\\ &= F_0 - 5F_2\end{aligned}$$

Continuing, we obtain

$$\begin{aligned}\langle 1^+ -1^- \rangle &= F_0 + F_2\\ \langle 1^- -1^+ \rangle &= F_0 + F_2\\ \langle 0^+0^- \rangle &= F_0 + 4F_2\end{aligned}$$

Substituting the results back into the results of the Slater sum rule (6-28), we have the term energies (apart from a common additive constant) given by

$$\begin{aligned}E(^1S) &= F_0 + 10F_2\\ E(^1D) &= F_0 + F_2\\ E(^3P) &= F_0 - 5F_2\end{aligned} \qquad (6\text{-}42)$$

Inspection of the definition of the F_k shows that they are all positive definite integrals. Thus our results are consistent with Hund's rules, which require the ^3P level to lie lowest. We note that the remaining terms also lie in the order suggested by the rule that maximum L lies lowest. In general, however, one can rely on the rules to give only the one lowest term correctly.

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[1] See Condon and Shortley, *op. cit.*, p. 180; an abbreviated table is given in Appendix C of this book.

To calculate the absolute values of these energies, we would need have good radial functions to evaluate the radial integrals F_k. Howev we can test the theory without knowing F_k by comparing ratios. F example,

$$\frac{E(^1S) - E(^1D)}{E(^1D) - E(^3P)} = \frac{9F_2}{6F_2} = \frac{3}{2}$$

The result should be independent of F_2 to the accuracy of our single-co figuration approximation. Experimental values for various np^2 atoms a 1.13, 1.14, 1.14, 1.48, 1.50, 1.39. The departures from 1.50 are largely du to the admixture of $np(n+1)p$ configurations. The general order-o magnitude agreement is not bad, though, and the terms at least fall in th proper order. For simplicity we shall usually be satisfied to use the single-configuration approximations for the L-S terms as the starting poin for considering fine and hyperfine structures. Before proceeding to tha however, let us examine the nature of these L-S eigen*functions* a bit mo directly.

6-8 Eigenfunctions and Angular-momentum Operations

In Sec. 6-6, we commented on the fact that only in simple cases are th individual determinants eigenfunctions of L, S as well as M_L, M_S. For example, (1^+1^-) has $L = 2$, $M_L = 2$, $S = M_S = 0$. However, by operatin on this determinant with L_-, we can find the combinations of determinant which form the partners of this function with $M_L = 1, 0, -1, -2$. Such operations can be considered simply as applications of our general formula for computing matrix elements of operators of the type F or G. Thus, for example,

$$L_-\Psi_A = \sum_B \Psi_B(B\,|L_-|\,A) \tag{6-43}$$

where $L_- = \sum_i L_-^i$. However, these angular-momentum operations occur so frequently that it is worthwhile to work out explicit results.

L_z and S_z. These operators are simple to handle since we have built our determinants out of eigenfunctions of L_z^i and S_z^i. Thus, when we operate with

$$L_z = \sum_{i=1}^{N} L_z^i = L_z^1 + L_z^2 + L_z^3 + \cdots + L_z^N$$

we obtain N determinants, each identical to the original one except for a factor m_l^i. Summing these, we have

$$L_z\Psi_A = \sum_i (m_l^i)\Psi_A = M_L\Psi_A \tag{6-44a}$$

Similarly,

$$S_z\Psi_A = \sum_i (m_s^i)\Psi_A = M_S\Psi_A \tag{6-44b}$$

and these determinants are shown to be eigenfunctions of L_z and S_z, as we have known all along.

$L_\pm$ **and** $S_\pm$. These are a bit more complicated, but using (6-13) it is easy to see that this works out to

$$L_\pm\Psi(n^1l^1m_l^{\,1}m_s^{\,1};\ldots) = \sum_i [l^i(l^i+1) - m_l^{\,i}(m_l^{\,i} \pm 1)]^{\frac12}\Psi(\ldots;n^il^i, m_l^{\,i}\pm 1, m_s^{\,i};\ldots) \qquad (6\text{-}45a)$$

and

$$S_\pm\Psi(n^1l^1m_l^{\,1}m_s^{\,1};\ldots) = \sum_i [(\tfrac34) - m_s^{\,i}(m_s^{\,i} \pm 1)]^{\frac12}\Psi(\ldots;n^il^im_l^{\,i}, m_s^{\,i}\pm 1;\ldots) \qquad (6\text{-}45b)$$

[Unlike (6-13), no $\pm$ signs appear here because we have not brought the resulting determinants to standard order.] Note that the only nonzero value of $[(\frac34) - m_s^{\,i}(m_s^{\,i} \pm 1)]$ is 1. This occurs when $m_s^{\,i} = \mp\frac12$. Also note that any Ψ's which are formally generated but which are inconsistent with the Pauli principle because of double occupancy of a spin-orbital function will vanish because of the antisymmetry of the determinants.

$\mathbf{L}^2$ **and** $\mathbf{S}^2$. We expand this as

$$\begin{aligned}\mathbf{L}^2 &= (\sum_i \mathbf{L}^i)^2 = \sum_i (\mathbf{L}^i)^2 + 2\sum_{i>j}\mathbf{L}^i\cdot\mathbf{L}^j \\ &= \sum_i l^i(l^i+1) + 2\sum_{i>j}L_z^{\,i}L_z^{\,j} + \sum_{i>j}(L_+^{\,i}L_-^{\,j} + L_-^{\,i}L_+^{\,j})\end{aligned}$$

The first two sums give diagonal matrix elements; the last one gives off-diagonal ones. The total effect of the operator is as follows:

$$\begin{aligned}L^2\Psi(n^1l^1m_l^{\,1}m_s^{\,1};\ldots) &= [\sum_i l^i(l^i+1) + 2\sum_{i>j}m_l^{\,i}m_l^{\,j}]\Psi(n^1l^1m_l^{\,1}m_s^{\,1};\ldots) \\ &\quad + \sum_{i\neq j}[l^i(l^i+1) - m_l^{\,i}(m_l^{\,i}+1)]^{\frac12}[l^j(l^j+1) - m_l^{\,j}(m_l^{\,j}-1)]^{\frac12} \\ &\quad \times \Psi(\ldots;n^i, l^i, m_l^{\,i}+1, m_s^{\,i};\ldots;n^j, l^j, m_l^{\,j}-1, m_s^{\,j};\ldots) \qquad (6\text{-}46a)\end{aligned}$$

Similarly, we have for the spin operators

$$\begin{aligned}S^2\Psi(n^1l^1m_l^{\,1}m_s^{\,1};\ldots) &= \left[\frac{3N}{4} + 2\sum_{i>j}m_s^{\,i}m_s^{\,j}\right]\Psi(n^1l^1m_l^{\,1}m_s^{\,1};\ldots) \\ &\quad + \sum_{i\neq j}[(\tfrac34) - m_s^{\,i}(m_s^{\,i}+1)]^{\frac12}[(\tfrac34) - m_s^{\,j}(m_s^{\,j}-1)]^{\frac12} \\ &\quad \times \Psi(\ldots;n^il^im_l^{\,i}, m_s^{\,i}+1;\ldots;n^jl^jm_s^{\,j}, m_s^{\,j}-1;\ldots)\end{aligned}$$

We can simplify the first term by noting that

$$\begin{aligned}2\sum_{i>j}m_s^{\,i}m_s^{\,j} &= \sum_i m_s^{\,i}\sum_{j\neq i}m_s^{\,j} = \sum_i m_s^{\,i}(M_S - m_s^{\,i}) \\ &= M_S^{\,2} - \sum_i (m_s^{\,i})^2 = M_S^{\,2} - \frac{N}{4}\end{aligned}$$

Thus the first coefficient is $[M_S^2 + N/2]$. Since the only nonzero value f the square roots is unity, the second term also can be simplified. If a spatial orbital is occupied by two electrons with paired spins, it appears in t second term with spins reversed, which produces just a sign change becau of the antisymmetry. This term cancels the contribution in the first ter of all paired spins. This leaves us with the result

$$\mathbf{S}^2\Psi_A = \left[M_S^2 + \frac{\text{number of unpaired spins}}{2}\right]\Psi_A + \sum \Psi_{A'} \qquad (6\text{-}46$$

where $\Psi_{A'}$ are all the determinants which differ from Ψ_A by a single inte change of spin orientations between distinct spatial orbitals.

Let us now apply this machinery to our np^2 example. Starting wit $\Psi(LM_LSM_S) = \Psi(2200) = (1^+1^-)$, we have

$$L_-\Psi(2200) = \sqrt{2 \cdot 3 - 2 \cdot 1}\,\Psi(2100) = 2\Psi(2100)$$

and

$$L_-\Psi(2200) = L_-(1^+1^-) = \sqrt{1 \cdot 2 - 1 \cdot 0}\,(0^+1^-) + \sqrt{1 \cdot 2 - 1 \cdot 0}\,(1^+0^-)$$

$$= \sqrt{2}[(0^+1^-) + (1^+0^-)]$$

Comparing, we have

$$\Psi(2100) = \frac{1}{\sqrt{2}}[(0^+1^-) + (1^+0^-)]$$

or, if the orbitals are returned to standard order,

$$\Psi(2100) = \frac{1}{\sqrt{2}}[(1^+0^-) - (1^-0^+)]$$

If we operated on this linear combination with $\mathbf{L}^2$, we could verify directly that it is in fact an eigenfunction satisfying

$$\mathbf{L}^2\frac{(1^+0^-) - (1^-0^+)}{\sqrt{2}} = 2 \cdot 3\,\frac{(1^+0^-) - (1^-0^+)}{\sqrt{2}}$$

The ease with which these matrix elements and eigenfunctions are found indicates another useful technique for reducing secular equations. We could, for example, easily compute matrix elements of $\mathbf{L}^2$ within the 3×3 $M_L = M_S = 0$ block which arises in the np^2 problem. If we diagonalized this $\mathbf{L}^2$ matrix by solving the simple secular equation, we would have found the three linear combinations belonging to ^1S, ^1D, ^3P, respectively, corresponding to eigenvalues 0, $2 \cdot 3$, $1 \cdot 2$. Exactly these linear combinations also must diagonalize the 3×3 matrix of the *Hamiltonian*, whose matrix elements are in general much harder to find. Although in the present case this method would be a bit more difficult than Slater's sum rule, it does play a very useful role in molecular calculations. In that case, one is often interested only in finding an $S = 0$ ground state. By first diagonalizing $\mathbf{S}^2$, one can find all the linear combinations of determinants which need to be considered in the final secular equation connecting several configurations.

6-9 Calculation of Fine Structure

We now take the eigenfunctions and eigenvalues found for the L-S terms as the starting point for introducing the *magnetic* or *relativistic* perturbations. These energies are of order $(v/c)^2$ smaller than the term separations; so for the lighter atoms it is satisfactory to consider the fine structure of each L-S term separately by perturbation theory. Because the various $M_L M_S$ substates of a term are degenerate, it is first necessary to organize linear combinations of them which are proper zero-order eigenfunctions such that there are no off-diagonal elements of the perturbation between them. This presents no difficulty, because we know that the total Hamiltonian including these spin-orbit coupling terms is invariant under rotations of the *total* system. Thus, according to the group theory, there are no matrix elements of H between states of different J and M_J. But the Wigner coefficients prescribe exactly what linear combinations of $M_L M_S$ states form the eigenfunctions of J, M_J. Thus they provide just the zero-order linear combinations which we require. Actually, we can usually get the eigen*values* by tricks which make even the Wigner coefficients unnecessary.

One-electron case. To get a start, we consider the simple case of a single electron moving in the spherical potential outside closed shells. The magnetic-perturbation energy of the spin can be expressed as

$$H' = -\boldsymbol{\mu}_S \cdot \mathbf{H}_{\text{eff}} = \frac{e\hbar}{mc}\,\mathbf{s} \cdot \left(\mathbf{E} \times \frac{\mathbf{v}}{c}\right) \tag{6-47}$$

where we have used the Lorentz transformation to find the effective magnetic field seen by the spin as it moves through the central electric field. This field may be expressed by

$$\mathbf{E} = -\frac{\partial V}{\partial r}\,\mathbf{r}_0 = \frac{1}{e}\frac{\partial U}{\partial r}\,\mathbf{r}_0$$

where $\mathbf{r}_0$ is a radial unit vector. Substituting this above, we have

$$H' = \frac{\hbar}{mc^2}\frac{\partial U}{\partial r}\,\mathbf{s} \cdot (\mathbf{r}_0 \times \mathbf{v}) = \frac{\hbar}{rm^2c^2}\frac{\partial U}{\partial r}\,\mathbf{s} \cdot (\mathbf{r} \times \mathbf{p}) = \frac{\hbar^2}{m^2c^2}\left(\frac{1}{r}\frac{\partial U}{\partial r}\right)\mathbf{l} \cdot \mathbf{s}$$

This simplified treatment has failed to introduce the factor of $\frac{1}{2}$ which results from the Thomas precession[1] of relativistic kinematics or from a

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[1] L. H. Thomas, *Nature*, **117**, 514 (1926).

straightforward reduction of the Dirac equation to a two-component f
Inserting this correction factor, we obtain

$$H' = \xi(r)\mathbf{l}\cdot\mathbf{s} \qquad \xi(r) = \frac{\hbar^2}{2m^2c^2}\frac{1}{r}\frac{\partial U}{\partial r} \qquad (6\text{-}$$

(Note that we take $\mathbf{l}$ and $\mathbf{s}$ in units of $\hbar$ making them dimension
quantities in these equations.)

When we deal with the many-electron problem, we shall simply genera
this to $H' = \sum_i \xi(r_i)\mathbf{l}_i\cdot\mathbf{s}_i$. This includes only the interaction of each s
with its own orbit. This is the dominant term since the central field
stronger than the interelectronic interaction. We thereby neglect the or
orbit, spin–other–orbit, and spin-spin terms. The effect of this neglect h
been considered by various authors.[1]

Matrix elements. In evaluating matrix elements of H', we take advant
of the fact that it is a product of three operators, each operating on co
pletely independent coordinates of the electron. $\xi(r)$ operates on the rad
coordinate, $\mathbf{l}$ on angular coordinates of the orbital position, and $\mathbf{s}$ on t
spin coordinates. This enables us to factor the matrix element as follow

$$(n'l'm_l'm_s\,|H'|\,nlm_lm_s) = (n'l'\,|\xi(r)|\,nl)(l'm_l'\,|\mathbf{l}|\,lm_l)\cdot(m_s'\,|\mathbf{s}|\,m_s) \qquad (6\text{-}4$$

Except for the radial integral, the other factors are elementary matr
elements which can be written down immediately. Since $\mathbf{l}$ is diagonal
$l, l' = l$. Noting that $\mathbf{l}\cdot\mathbf{s}$ is a scalar operator, we know that ΔM
$(m_l' + m_s') - (m_l + m_s)$ must be zero. Since $\mathbf{l}$ and $\mathbf{s}$ separately are vect
operators, they have $\Delta m_l = \pm 1, 0$ and $\Delta m_s = \mp 1, 0$ selection rules. Th
we conclude that l and $m = m_l + m_s$ are good quantum numbers but m
and m_s are not. Instead, we know by our general arguments of rotation
invariance that $|\mathbf{j}| = |\mathbf{l} + \mathbf{s}|$ is now a good quantum number. This f
enables us to get our answer by a short cut requiring almost no calculatio

We note that

$$\mathbf{j}^2 = (\mathbf{l} + \mathbf{s})^2 = \mathbf{l}^2 + \mathbf{s}^2 + 2\mathbf{l}\cdot\mathbf{s}$$

Therefore

$$\mathbf{l}\cdot\mathbf{s} = \frac{\mathbf{j}^2 - \mathbf{l}^2 - \mathbf{s}^2}{2} \qquad (6\text{-}5$$

This is a quantum-mechanical operator equation. Since, in the represe
tation based on the actual eigenfunctions fixed by the Wigner coefficien
$\mathbf{j}^2$, $\mathbf{l}^2$, $\mathbf{s}^2$ are all diagonal, $\mathbf{l}\cdot\mathbf{s}$ also has only diagonal elements in t
representation and these can be written down by inspection. Thus we co
clude that

$$E(nljm) = E_0(nl) + \zeta(nl)(ljm\,|\mathbf{l}\cdot\mathbf{s}|\,ljm)$$

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[1] For example, see R. E. Trees, *Phys. Rev.*, **82**, 683 (1951); H. H. Marvin, *Phys. Rev.*, **7**
102 (1947); R. G. Breene, Jr., *Phys. Rev.*, **119**, 1615 (1960).

or
$$E(nljm) = E_0(nl) + \frac{\zeta(nl)}{2}\,[j(j+1) - l(l+1) - s(s+1)] \tag{6-51}$$

where $\zeta(nl) = \int_0^\infty R_{nl}^2(r)\xi(r)\,dr$ is the appropriate radial integral.

Now, for a single electron, we have $s = \frac{1}{2}$ and $j = l \pm \frac{1}{2}$. Inserting these values in (6-51) leads to

$$E(nljm) = E_0(nl) + \zeta(nl)\begin{cases} \dfrac{l}{2} \\ \dfrac{-(l+1)}{2} \end{cases} \quad \text{for } j = \begin{cases} l + \dfrac{1}{2} \\ l - \dfrac{1}{2} \end{cases} \tag{6-52}$$

For all reasonable potentials, $\partial U/\partial r > 0$; so $\zeta > 0$. Thus *the state of lower j lies lowest, as required by the Hund rule.* This fact could, of course, be confirmed by an elementary consideration of the direction of $\mathbf{H}_{\text{eff}}$ relative to the orientation of the orbit. The doublet separation $(l + \frac{1}{2})\zeta(nl)$ is clearly of magnetic origin and smaller than electronic energies by a factor of order α^2. For example, the sodium D lines at 17,000 cm^{-1} result from the transition $3p \rightarrow 3s$. The $3p$ term is split into ${}^2P_{\frac{3}{2}}$ and ${}^2P_{\frac{1}{2}}$ with a separation $3\zeta/2$ of 17 cm^{-1}. This splitting is mirrored in the splitting of the optical transition into a doublet with this separation, which amounts to 0.1 per cent in this case.

Many-electron case. Here we take our perturbing term to be

$$H' = \sum_i \xi(r_i)\mathbf{l}_i \cdot \mathbf{s}_i$$

The presence of more than one electron complicates the calculation of matrix elements. This occurs because $\mathbf{l}_i$ and $\mathbf{s}_i$ are now only ordinary vector operators with respect to rotations of space and spin coordinates, whereas in the one-electron case they were the total angular momentum corresponding to these respective rotations. Thus, whereas $\mathbf{l}$ and $\mathbf{s}$ were diagonal in l and s for one electron, the Wigner-Eckart theorem (Sec. 5-12) tells us that $\mathbf{l}_i$ and $\mathbf{s}_i$ will have matrix elements of the type $\Delta L = \pm 1$, $\Delta S = \pm 1$ as well as $\Delta L = \Delta S = 0$, in the general case. However, as long as ζ is small compared with term separations, the simple L-S coupling scheme is still a good approximation. Thus we shall ignore the effects of admixtures of other L and S values by the spin-orbit coupling, and consider only the matrix elements within a given term, i.e., those elements which are diagonal in L and S.

For these, we can take advantage of the fact, noted in Sec. 5-12, that the matrix elements of a vector operator are proportional to those of the corresponding angular momentum. Noting that $\xi(r)$ is a scalar, we may include it with no change in transformation properties. Thus, using n to denote all quantum numbers specifying the configuration, we have

$$(nLM'_LSM'_S\,|\xi(r_i)\mathbf{l}_i\cdot\mathbf{s}_i|\,nLM_LSM_S)$$
$$=(nLM'_L\,|\xi(r_i)\mathbf{l}_i\,|nLM_L)\cdot(nSM'_S|\,\mathbf{s}_i|\,nSM_S)$$
$$=(nL\,\|\xi(r_i)l_i\|\,nL)(nS\,\|s_i\|\,nS)(LM'_L\,|\mathbf{L}|\,LM_L)\cdot(SM'_S\,|\mathbf{S}|\,S$$

If we now sum over all the electrons, we have

$$(nLM'_LSM'_S\,|H'|\,nLM_LSM_S)=\zeta(nLS)(LM'_LSM'_S\,|\mathbf{L}\cdot\mathbf{S}|\,LM_LSM_S)\qquad(6\text{-}$$

where $$\zeta(nLS)=\sum_i(nL\,\|\xi(r_i)l_i\|\,nL)(nS\,\|s_i\|\,nS)$$

Thus, *within an L-S term*, the matrix elements of $\sum_i\xi(r_i)\mathbf{l}_i\cdot\mathbf{s}_i$ are proportio to those of $\mathbf{L}\cdot\mathbf{S}$. This is an operator equation, since we have shown it to true for a general element (within the term). Since operator equations invariant under a unitary transformation, this result also holds in the *LS* representation based on the proper zero-order eigenfunctions. Thus can write down our energy eigenvalues by inspection, just as in the o electron case, obtaining

$$E(nLSJM)=E_0(nLS)+\zeta(nLS)\frac{J(J+1)-L(L+1)-S(S+1)}{2}\quad\blacktriangleright\ (6\text{-}$$

The result is exact for the Hamiltonian used, within the approximati that we neglect the effects of coupling to other terms. These effects c be taken into account by using the Racah coefficients to handle the ter off-diagonal in L and S. In fact Racah was led to develop his method from consideration of problems of this type.

Lande interval rule. For the time being, $\zeta(nLS)$ is considered merely a parameter which will be evaluated shortly. The theory can be tested its present form by considering ratios of separations of levels. The se aration of Jth and $(J-1)$st level is

$$E(nLSJM)-E(nLS,J-1,M)=\left(\frac{\zeta}{2}\right)[J(J+1)-(J-1)J]=\zeta(nLS)J\qquad(6\text{-}5$$

Thus the separations of adjacent multiplet levels should be proportion to the higher of the J values concerned. This is the *Lande interval rul*

As an example showing how well this holds, we cite some data on th $3d^64s^2\,{}^5D$ term of iron in Table 6-2. If the rule were rigorously true, th entries in the last column would all be equal. The deviations represent th effect of the smaller interaction terms, which we have omitted.

One can readily see that the center of gravity of the levels of a multipl [each level being weighted with its statistical weight $(2J+1)$] is exactl where it would be in the absence of spin-orbit effects. This follows fro invariance of the diagonal sum and the fact that the diagonal values of H' in an LSM_LM_S representation are ζM_LM_S. Thus

$$H'_{\text{av}} = [\zeta/(2L+1)(2S+1)]\sum_{-L}^{L} M_L \sum_{-S}^{S} M_S = 0$$

This fact was used to determine suitable average energies for terms in checking the predictions on the L-S-term separations in Sec. 6-7.

Table 6-2

Multiplet intervals in the ${}^5D$ terms of iron

Level	*Energy, cm^{-1}*	*Interval*	*ζ = interval/J*
${}^5D_4$	0.0	−415.9	−103.9
${}^5D_3$	415.9	−288.1	−96.1
${}^5D_2$	704.0	−184.1	−92.1
${}^5D_1$	888.1	−89.9	−89.9
${}^5D_0$	978.1		

Absolute term intervals. The Landé interval rule was obtained effortlessly by group theory. However, to evaluate actual magnitudes of energy splittings, we always must evaluate some parameter or radial integral about which the group theory gives no information. We now seek to evaluate the parameter $\zeta(nLS)$, which gives the scale factor for the fine structure of a given L-S term. We can reduce this parameter to simple integrals by a method similar to the Slater-sum-rule method for calculating term separations.

The method is based on comparing two alternative expressions for the same matrix element. For a diagonal element, our foregoing discussion allows us to write

$$\begin{aligned}(nLSM_LM_S|\sum_i \xi(r_i)\mathbf{l}_i\cdot\mathbf{s}_i|\,nLSM_LM_S) &= \zeta(nLS)(LSM_LM_S|\mathbf{L}\cdot\mathbf{S}|\,LSM_LM_S)\\ &= \zeta(nLS)M_LM_S \qquad (6\text{-}56a)\end{aligned}$$

But, by our rule for evaluating diagonal elements of operators of type $F = \sum_i f_i$ over determinantal wave functions, we also know that this matrix element must have the value

$$\sum_i (a^i|\xi(r)\mathbf{l}\cdot\mathbf{s}|\,a^i) = \sum_i \zeta(n^il^i)m_l^i m_s^i \qquad (6\text{-}56b)$$

where $\zeta(nl)$ are the same integrals as those defined in handling the one-electron problem. This allows a straightforward evaluation of $\zeta(nLS)$ as long as there is only a single determinant having the given M_L, M_S values.

For example, in our np^2 case, the only $M_L = M_S = 1$ determinant is $(1^+$
This belongs to the ${}^3P$ term. Applying the equality above,

$$\zeta(np^2, {}^3P) = \frac{1}{M_L M_S} \sum_i \zeta(n^i l^i) m_l^i m_s^i = \zeta(np) \cdot 1 \cdot \frac{1}{2} + 0 = \frac{\zeta(np)}{2}$$

If there is more than one determinant from the configuration un consideration having given M_L, M_S, we extend this method, using the variance of diagonal sums under a unitary transformation, to write

$$M_L M_S \sum_{\text{terms}} \zeta(nLS) = \sum_{\text{det}} \left[\sum_i \zeta(n^i l^i) m_l^i m_s^i \right] \qquad (6\text{-}$$

The sums over both terms and determinants are to run over the given M_L block of the table (such as Table 6-1) pertaining to the given configurati By a stepwise procedure like that in Slater's sum-rule method, the ζ val for all terms can be found. Our np^2 example is too simple to provide useful example, since the only multiple entries in Table 6-1 are in $M_S =$ blocks. However, if we consider two *inequivalent p* electrons $(npn'p)$, can set up an illustration. The determinant (1^+1^+) belongs to ${}^3D$ wi $M_L = 2, M_S = 1$. Using the simple method, we obtain $\zeta(npn'p\,{}^3D)$ $\frac{1}{4}[\zeta(np) + \zeta(n'p)]$. Now, proceeding to the $M_L = M_S = 1$ block, we fi two determinants: (1^+0^+) and (0^+1^+). Suitable combinations of the belong to the terms ${}^3D$ and ${}^3P$. Using (6-57), we equate

$$\zeta(npn'p\,{}^3D) + \zeta(npn'p\,{}^3P) = \tfrac{1}{2}\zeta(np) + \tfrac{1}{2}\zeta(n'p)$$

By subtraction, we then find

$$\zeta(npn'p\,{}^3P) = \zeta(npn'p\,{}^3D) = \frac{[\zeta(np) + \zeta(n'p)]}{4} \qquad (6\text{-}5$$

As an experimental test, consider the $2p3p$ configuration of atom carbon. There it is found that $\zeta({}^3D) = 11.2$, $10.6\ \text{cm}^{-1}$ and $\zeta({}^3P) = 10.2$ $12.5\ \text{cm}^{-1}$, the alternative values being evaluated from different multipl intervals. We see that in fact $\zeta({}^3D) \simeq \zeta({}^3P)$, and we also note that th interval rule is quite well satisfied.

Configurations of the form nl^x and Hund's rules. An important speci case in atomic structure is that in which all electrons not in closed shell belong to a single subshell and we are interested in the ground term. Ac cording to the first two Hund rules, this term will have the largest values o S and L consistent with the exclusion principle. For such states the bloc with $M_L = L$ and $M_S = S$ always contains but a single determinant, an we may evaluate $\zeta(nLS)$ very easily. We distinguish two cases.

1. Shell less than half full ■ Here all the spins *can* be parallel, and i the ground state they *will* be, by Hund's first rule. For example, for $3d$

the ground term is ${}^5D$, and we have $(2^+1^+0^+ -1^+)$ for the determinant with $M_L = L = 2$, $M_S = S = 2$. In general, we have from (6-56)

$$M_L M_S \zeta(nLS) = \zeta(nl) \sum_i m_l^i m_s^i$$

In our special case this becomes

$$LS\zeta(nLS) = \zeta(nl) \cdot \frac{1}{2} \cdot \sum_i m_l^i = \frac{\zeta(nl)M_L}{2} = \frac{\zeta(nl)L}{2}$$

Therefore $$\zeta(nl^x, LS) = \frac{\zeta(nl)}{2S} \qquad x < 2l + 1 \tag{6-59a}$$

2. Shell more than half full ▪ In this case, some spins must be reversed to satisfy the Pauli principle. For example, in the $3d^6\,{}^5D$ ground term,

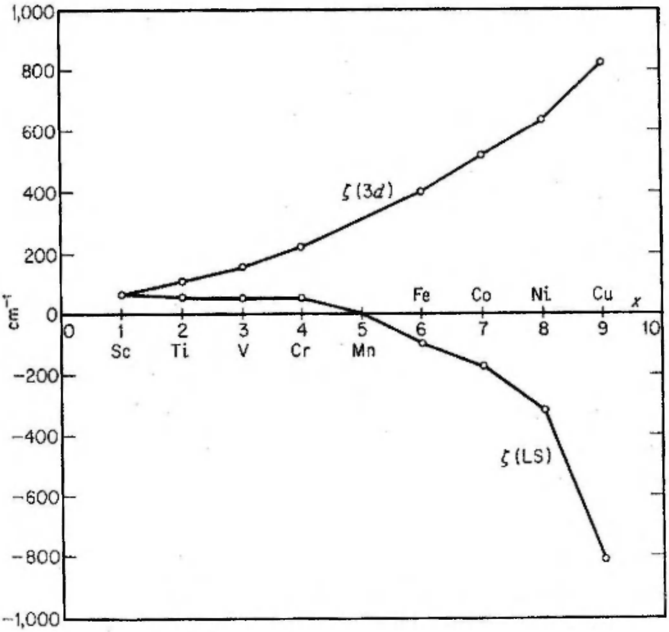

Fig. 6-2. *Spin-orbit parameters in $3d^x$ transition elements. The splitting parameters $\zeta(LS)$ are computed as indicated in Table 6-2 and averaged over the various splittings. The data used are for the $3d^x4s^2$ configurations of the neutral atoms. (From Charlotte E. Moore, "Atomic Energy Levels," Natl. Bur. Standards, Circ. 467, vols. I and II, 1949 and 1952. A very similar figure appears in Condon and Shortley.)*

$(2^+1^+0^+ -1^+ -2^+2^-)$ is the determinant for the $M_L = M_S = 2$ state. general, we have for this type of case,

$$M_L M_S \zeta(nLS) = LS\zeta(nLS) = \zeta(nl)\left\{\frac{1}{2}\sum_{-l}^{l} m_l{}^i - \tfrac{1}{2}M_L\right\} = \frac{-\zeta(nl)L}{2}$$

Thus
$$\zeta(nl^x, LS) = \frac{-\zeta(nl)}{2S} \qquad x > 2l + 1 \tag{6-59}$$

Comparing (6-59*a*) and (6-59*b*), we see that the sign of the effective spi orbit parameter $\zeta(nl^x, LS)$ changes from a positive to a negative value if th shell is more than half full. This causes the state of lowest energy to chang from minimum J to maximum J in this case, as required by the third Hun rule. In case $x = 2l + 1$, so that the shell is exactly half full, $S = (2l + 1)/$ but $L = 0$. Thus $J = S = (2l + 1)/2$ only, and there is no multiplet struc ture. Hence no rule is required for this case.

Example: $3d^x$. In Fig. 6-2, we plot the values of $\zeta(3d)$ and $\zeta(LS)$ versu x for the atoms of the iron transition series. Note that $\zeta(LS)$ is initially nearly constant, then changes sign and increases rapidly. On the other hand, $\zeta(3d)$ stays positive and increases steadily in magnitude with Z and hence $(\partial U/\partial r)$, as expected from (6-48).

This situation is of particular importance in understanding electronic spin resonance experiments on iron-group salts. In this case, the g factor is shifted from the free-electron value (2.0023) by second-order effects of the spin-orbit coupling proportional to $-\zeta(LS)$. Thus for the first half of the shell (for example, Cr, V) $g < 2$, but it is close to 2, since ζ is small. For the second half of the shell (for example, Fe, Ni, Cu) g exceeds 2.0023 by an amount which increases rapidly with $\zeta(LS)$.

6-10 Zeeman Effect

With the inclusion of the relativistic, or spin-orbit, coupling terms in the Hamiltonian in the previous section, we have reduced the atomic degeneracy to the full extent consistent with the rotational invariance of the problem. This invariance requires all $M (= M_J)$ states belonging to a given fine-structure level (J) to be degenerate, because there are rotational-symmetry operations that take states with one M value into states with another. This residual degeneracy is completely lifted by applying a magnetic field **H**, which destroys the isotropy of space by introducing a preferred direction. The remaining symmetry is only the group of two-dimensional rotations about **H**, which, being Abelian, has only one-dimensional representations. Hence all degeneracy is lifted, and, as discussed in Sec. 3-7, states are characterized by their M value, such that rotation by an angle φ about **H** multiplies the function by $e^{-iM\varphi}$. We now calculate the magnitude of the splitting of the energy levels produced by the applied field.

The perturbing Hamiltonian for a magnetic field **H** in the z direction is

$$H_Z = -\boldsymbol{\mu} \cdot \mathbf{H} = \beta(L_z + g_s S_z)\mathrm{H} \qquad (6\text{-}60)$$

where μ is the magnetic moment of the atom, β is the Bohr magneton, L and S are the orbital and spin angular momenta in units of $\hbar$, and g_s is the anomalous g value of the electron spin. According to the usual derivation from the Dirac equation,[1] g_s is exactly 2, as had been found empirically from spectra. However, in 1948, Schwinger[2] showed that, to first order in $\alpha = e^2/\hbar c \approx \frac{1}{137}$, g_s should have the value $2(1 + \alpha/2\pi) = 2.0023$. This small correction arises from quantum electrodynamic effects which enter from treating the electromagnetic field in vacuum as a quantum-mechanical system with which the electron interacts. This calculation was carried to higher order by Karplus and Kroll,[3] who obtained $g_s = 2.002291$. This calculation was later corrected by Sommerfield,[4] who found $g_s = 2.002319$. Precise atomic-beam experiments confirm this value quite well. Actually, many other relativistic corrections enter when the electron is moving in an atom, but these require more specific individual treatment for each atom.[5] Since these corrections are outside the scope of our treatment, we shall simply take g_s as a given quantity, slightly larger than 2. We shall also neglect the terms in the Hamiltonian which involve the square of the magnetic vector potential, since these are ordinarily negligible compared with the linear terms.

Weak-field limit. For weak magnetic fields, the matrix elements of H_Z are so small compared with the separation between multiplet levels with different values of J that we can restrict our attention to matrix elements diagonal in J. Noting that both **L** and **S** transform as vectors, we may use the Wigner-Eckart theorem, and in particular the vector matrix elements of (5-69), to write that

$$\begin{aligned} (JM'|\mathbf{L}|JM) &= (J\|L\|J)(JM'|\mathbf{J}|JM) \\ \text{and} \qquad (JM'|\mathbf{S}|JM) &= (J\|S\|J)(JM'|\mathbf{J}|JM) \end{aligned} \qquad (6\text{-}61)$$

We can evaluate the reduced matrix elements by a simple argument. First, noting that $\mathbf{L} + \mathbf{S} = \mathbf{J}$, we see that $(J\|L\|J) + (J\|S\|J) = 1$. For convenience in writing, let $(J\|S\|J) = \alpha$. Then $(J\|L\|J) = 1 - \alpha$. Now note that $\mathbf{L}^2 = (\mathbf{J} - \mathbf{S})^2 = \mathbf{J}^2 + \mathbf{S}^2 - 2\mathbf{J} \cdot \mathbf{S}$. If we take the $|LSJM)$ diagonal element of this equation, we have

$$L(L + 1) = J(J + 1) + S(S + 1) - 2\alpha J(J + 1)$$

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[1] P. A. M. Dirac, "The Principles of Quantum Mechanics," 3d ed., chap. XI, Oxford University Press, New York, 1947.

[2] J. Schwinger, *Phys. Rev.*, **73**, 416 (1948); **76**, 790 (1949).

[3] R. Karplus and N. M. Kroll, *Phys. Rev.*, **77**, 536 (1950).

[4] C. M. Sommerfield, *Phys. Rev.*, **107**, 328 (1957).

[5] See, for example, A. Abragam and J. H. Van Vleck, *Phys. Rev.*, **92**, 1448 (1953).

Solving for α, we obtain

$$\alpha = (J \| S \| J) = \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

(6-

and $$1 - \alpha = (J \| L \| J) = \frac{J(J+1) - S(S+1) + L(L+1)}{2J(J+1)}$$

By using (6-61) and (6-62), (6-60) becomes

$$H_Z = [(1 - \alpha) + g_s\alpha]\beta J_z \mathsf{H} \equiv g_J \beta J_z \mathsf{H} \qquad \text{(6-6}$$

which defines the g_J factor. Since $J_z = M$ is diagonal in our representatio (6-63) directly gives the eigenvalues of the magnetic perturbation.

$$E_M = g_J \beta M \mathsf{H} \qquad \text{(6-6}$$

These are to be added to the field-free energy level. Note that, if g_s is se equal to exactly 2, g_J becomes $(1 + \alpha)$. This is the usual expression du to Lande, namely,

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \qquad \text{(6-65)}$$

Though usually obtained in elementary courses by nonrigorous means, we see that this is a rigorous result of our group theory, provided that we tak $g_s = 2$.

Strong-field limit (Paschen-Back effect). Since **L** and **S** are vector operators, they have $\Delta J = \pm 1$ matrix elements in addition to the $\Delta J = 0$ elements used above. In very strong fields $[\beta \mathsf{H} \gg \zeta(LS)]$, these matrix elements are more important energetically than the spin-orbit coupling which couples **L** and **S** to form **J**, giving the fine-structure splittings. In this case, we abandon the $|LSJM)$ basis functions, suitable to field free space, and revert to the $|LM_LSM_S)$ functions. The latter are suitable zero-order functions for a strong field which "decouples" **L** from **S**, leaving both precessing about **H**. The diagonal matrix elements of H_Z can be written down directly as

$$H_Z = \beta \mathsf{H}(M_L + g_s M_S) \qquad \text{(6-66)}$$

This is the first-order magnetic energy. However, we must remember that the spin-orbit coupling is still present. From (6-53), it can be written

$$H_{S\text{-}O} = \zeta \mathbf{L} \cdot \mathbf{S} = \zeta[L_z S_z + \tfrac{1}{2}(L_+ S_- + L_- S_+)] \qquad \text{(6-67)}$$

Adding the diagonal terms of (6-67) to (6-66), we have for the first-order energy

$$E(M_L, M_S) = \zeta M_L M_S + \beta \mathsf{H}(M_L + g_s M_S) \qquad \text{(6-68)}$$

This will describe the very strong field limit (complete Paschen-Back effect).

Typically fields of 10^6 gauss are required to reach this limit, because $\zeta \sim 100\ \text{cm}^{-1}$. Thus this limit can be observed only in relatively light atoms, where ζ is small.

Intermediate-field region (incomplete Paschen-Back effect). When $\beta\mathrm{H} \sim \zeta$, neither limiting approximation is valid, and we must deal with off-diagonal as well as diagonal matrix elements, regardless of our choice of quantization scheme. Clearly $M = M_L + M_S$ must remain a rigorous quantum number throughout, because of rotational invariance about the field direction. However, if we use the $M_L M_S$ quantization scheme, for example, though H_Z is diagonal, $H_{S\text{-}O}$ has elements of the form $\Delta M_L = \pm 1$, $\Delta M_S = \mp 1$, as well as the diagonal elements used above. From (6-67), we see that these elements are

$$(M_L \pm 1, M_S \mp 1 \,|H_{S\text{-}O}|\, M_L, M_S) = \frac{\zeta}{2}[L(L+1) - M_L(M_L \pm 1)]^{\frac{1}{2}}[S(S+1) - M_S(M_S \mp 1)]^{\frac{1}{2}} \qquad (6\text{-}69)$$

Using them in second-order perturbation theory, we can extend the usefulness of the high-field limit downward.

On the other hand, if we use JM quantization, $H_{S\text{-}O}$ is diagonal and $H_Z = \beta\mathrm{H}[J_z + (g_s - 1)S_z]$ has a diagonal part (in J_z) and a part (in S_z) which has $\Delta J = \pm 1$ matrix elements as well as diagonal ones. These may be found by specializing (5-84), which involves a simple application of Racah coefficients (see Exercise 5-11). Using these elements, perturbation theory will give the departures from a linear Zeeman effect which set in when the Zeeman splitting ($\sim\beta\mathrm{H}$) begins to become comparable with the multiplet interval ($\sim\zeta$).

When more accurate solutions are required than can be obtained by perturbation theory, a secular equation must be solved exactly for the eigenvalues. Note that, since $M = J_z$ remains a valid quantum number (representation label) throughout, the secular equation will be between only the zero-order states having a given M value. This will at most be the number of levels in the multiplet, namely, $(2S + 1)$ or $(2L + 1)$, whichever is smaller. If we have $S = \frac{1}{2}$, there is never more than a 2×2 to solve and we may solve the problem algebraically. For illustration, consider the states with $M = M_L' + \frac{1}{2}$. The Hamiltonian matrix connecting the zero-order states with $(M_L, M_S) = (M_L', \frac{1}{2})$ and $(M_L' + 1, -\frac{1}{2})$ is

$$\begin{bmatrix} \dfrac{\zeta M_L'}{2} + \beta\mathrm{H}\left(M_L' + \dfrac{g_s}{2}\right) & \dfrac{\zeta}{2}[L(L+1) - M_L'(M_L'+1)]^{\frac{1}{2}} \\ \dfrac{\zeta}{2}[L(L+1) - M_L'(M_L'+1)]^{\frac{1}{2}} & \dfrac{-\zeta(M_L'+1)}{2} + \beta\mathrm{H}\left(M_L' + 1 - \dfrac{g_s}{2}\right) \end{bmatrix} \qquad (6\text{-}70)$$

The solutions of the secular equation are then [after substituting M fo $(M_L' + \frac{1}{2})$]

$$E_{\pm} = \beta \mathsf{H} M - \frac{\zeta}{4} \pm \frac{\zeta}{2} \left\{ \left(L + \frac{1}{2} \right)^2 + \frac{2\beta \mathsf{H} M}{\zeta} (g_s - 1) + \frac{\beta^2 \mathsf{H}^2}{\zeta^2} (g_s - 1)^2 \right\}^{\frac{1}{2}} \tag{6-71}$$

It is easily verified that this expression reduces correctly to the limitin values derived earlier, both when $\beta\mathsf{H} \gg \zeta$ and when $\beta\mathsf{H} \ll \zeta$. To illustrat

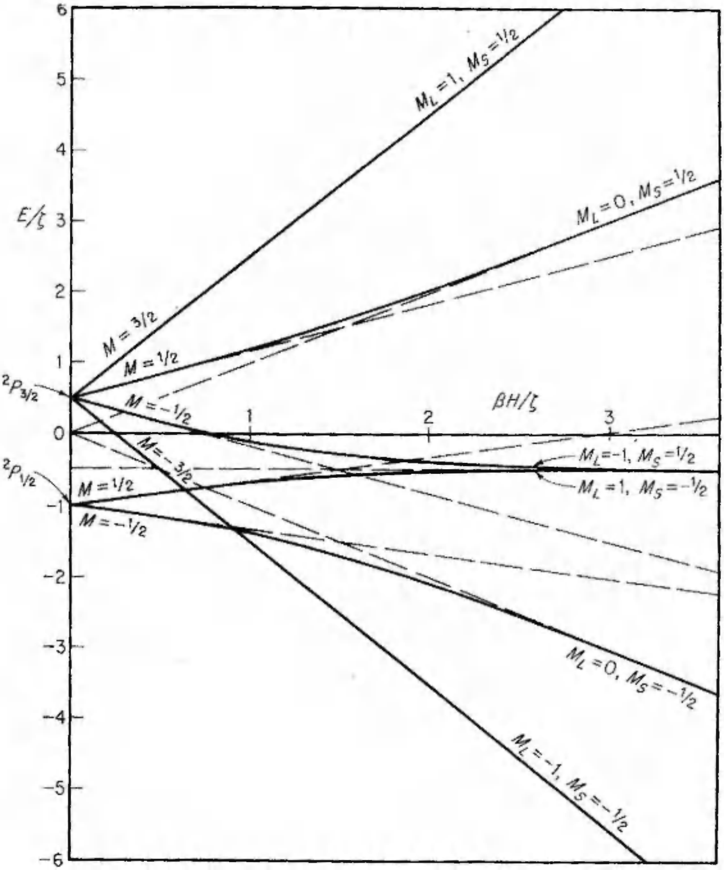

Fig. 6-3. *Transition to Paschen-Back region for ^2P term (schematic).*

the transition from the weak to strong-field limit, in Fig. 6-3 we graphically display the result (6-71) for the special case of $L = 1$. In other words, we show the splitting of the levels of a ^2P state in a magnetic field. The dashed lines indicate the extrapolation of the low-field linear Zeeman effect which would occur if the Paschen-Back effect did not set in. Dashed lines are also used to indicate the extrapolation of the high-field limit down to zero field.

Spectra. The energy-level structure having been worked out, the observed spectrum is determined provided that one knows the selection rules. These are fixed by the matrix elements of vector operators for the usual dipole transitions and were discussed in Sec. 5-12. The results are that $\Delta M = 0$ for radiation polarized along $\mathbf{H}$ and $\Delta M = \pm 1$ for radiation polarized perpendicular to $\mathbf{H}$. The latter two can be separated by using circularly polarized radiation in the + and − senses.

If a transition is induced between the Zeeman-split sublevels of a single multiplet level, it will be a *magnetic*-dipole transition, because the parities of initial and final states are the same. In this case, it is the polarization of the high-frequency magnetic field that enters in the selection rule (and the frequency will typically be in the microwave range). However, if the transition is an ordinary optical one between levels of different parity, the selection rules are governed by the polarization of the optical-frequency electric field and the effect of the magnetic field is only to produce a small splitting of the line into closely spaced components. The latter case is, of course, what is commonly referred to as the Zeeman effect.

6-11 Magnetic Hyperfine Structure

According to our group theory, in the absence of external fields, we expect J to be a rigorous quantum number and the degeneracy of the $(2J + 1)$ states in a level to be absolute. Yet when atomic spectra are observed, one often finds that the fine-structure lines split even further into *hyperfine structure* (h.f.s.). Since group theory allows no such splitting from the electronic degrees of freedom, it must result from an additional degree of freedom. Pauli (1924) suggested that, if the nucleus had a spin, it could provide this. The extra structure is then associated with the new irreducible representations of the full rotation group based on the direct product of nuclear and electronic eigenfunctions.

The energetic interaction which produces the splitting can be either electric or magnetic, the most important terms being the electric-quadrupole and magnetic-dipole interactions. As is well known, parity is conserved to a very high order under all the strong nuclear interactions, and therefore for most purposes parity is a good nuclear quantum number. This prevents the nucleus from having a permanent (i.e., diagonal) electric-dipole moment, because matrix elements of such a polar vector must vanish between states of the same parity. The same argument excludes all the odd electric multipoles. (The parity-violating weak interactions produce electric-dipole moments far too small to be detected.) Since the magnetic-dipole moment is an axial vector, there is no rule against the existence of permanent magn dipole moments.

The parity considerations also allow magnetic-octupole, -32-pole, moments. However, the magnitude of the effect falls rapidly with incre multipole order so that only relatively recently has even an octupole e been measured.[1] We shall confine our attention to the dipole interac where the Hamiltonian is simply

$$H_m = -\boldsymbol{\mu}_I \cdot \mathbf{H}_{\text{eff}} = -\boldsymbol{\mu}_I \cdot (\mathbf{H}_0 + \mathbf{H}_J) \qquad (6$$

where $\mathbf{H}_0$ is any externally applied field and $\mathbf{H}_J$ is the field at the nucl produced by the electronic motion of the atom indicated by its angu momentum **J**.

It is convenient to express the nuclear dipole moment $\boldsymbol{\mu}_I$ as

$$\boldsymbol{\mu}_I = \left(\frac{\mu}{I}\right)\mathbf{I}$$

where μ and I are the tabulated moment and spin of the nucleus. T nuclear moment μ can be determined by measuring the energy-level sep ration in a known external field $\mathbf{H}_0$, provided that we can make a suita allowance for $\mathbf{H}_J$. Now, since $\mathbf{H}_J$ must transform as a vector under rot tions of the electronic wavefunction, its matrix elements can be found using the Wigner-Eckart theorem. In particular, since the h.f.s. energi are so small compared with the fine-structure energies separating stat of different J, we usually need consider only elements of $\mathbf{H}_J$ diagonal in But, as we have noted before, such matrix elements are proportional to tho of **J** itself. Thus we have

$$(JM'\,|\mathbf{H}_J|\,JM) = A(JM'\,|\mathbf{J}|\,JM)$$

We evaluate A by postmultiplying both sides by the matrix operator This leads to

$$A = \frac{(JM\,|\mathbf{H}_J \cdot \mathbf{J}|\,JM)}{(JM\,|\mathbf{J} \cdot \mathbf{J}|\,JM)} = \frac{(JM\,|\mathbf{H}_J \cdot \mathbf{J}|\,JM)}{J(J+1)}$$

Therefore, in the absence of an external field, (6-72) becomes

$$H_m = a\mathbf{I} \cdot \mathbf{J} \qquad ▶ (6\text{-}73$$

with

$$a = -\frac{\mu_I(JM\,|\mathbf{H}_J \cdot \mathbf{J}|\,JM)}{IJ(J+1)} \qquad (6\text{-}73$$

With this result in hand, we have reduced the magnetic h.f.s. proble to a form identical with the spin-orbit interaction, which we have alread lved. If we define a total angular momentum $\mathbf{F} = \mathbf{I} + \mathbf{J}$, we have

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[1] V. Jaccarino, J. G. King, R. A. Satten, and H. H Stroke, *Phys. Rev.*, **94**, 1798 (1954)

$$\mathbf{I}\cdot\mathbf{J} = \tfrac{1}{2}(\mathbf{F}^2 - \mathbf{I}^2 - \mathbf{J}^2)$$

and hence

$$E(nLSJIF) = E_0(nLSJI) + \left(\frac{a}{2}\right)[F(F+1) - J(J+1) - I(I+1)] \qquad (6\text{-}74)$$

The Lande interval rule becomes

$$E(F) - E(F-1) = aF \qquad (6\text{-}75)$$

This should hold with excellent accuracy because I and J are *very* near to rigorous quantum numbers. The breakdown is proportional to $(a/\Delta E)$, where ΔE is the energy separation from a state of different J (or I) which is coupled to the state under consideration by $\Delta J = \pm 1$ (or $\Delta I = \pm 1$) matrix elements of the complete Hamiltonian. Since $a \sim 0.1\ \text{cm}^{-1}$, while $\Delta E \sim \zeta(LS) \sim 100\ \text{cm}^{-1}$, this error should be very small. Since the ΔE for a change of I is in the nuclear energy (millions of electron volts) range, such effects are completely negligible. Any deviation from the Lande interval rule (after correcting for the small admixtures of states with $J \pm 1$) must be ascribed to the higher multipoles, principally the electric-quadrupole interaction.

Calculation of a for non-S-states. In order to use this result to determine μ, we must be able to calculate a from the atomic wavefunction. The most obvious contribution to $\mathbf{H}_J$, and hence a, is the magnetic field produced by the orbital currents about the nucleus,

$$\mathbf{H}_L = \sum_i \frac{e}{c}\frac{\mathbf{v}_i \times \mathbf{r}_i}{r_i^3} = \frac{e}{mc}\sum_i \frac{\mathbf{p}_i \times \mathbf{r}_i}{r_i^3} = -2\beta \sum_i \frac{\mathbf{l}_i}{r_i^3} \qquad (6\text{-}76)$$

where we measure $\mathbf{l}_i$ in units of $\hbar$ and β is the Bohr magneton.

The dipole-dipole interaction between the nuclear moment and the electronic spins may be expressed as

$$H_{dd} = -\boldsymbol{\mu}_I \cdot \mathbf{H}_S \qquad (6\text{-}77a)$$

where

$$\mathbf{H}_S = 2\beta \sum_i \frac{1}{r_i^3}\left[\mathbf{s}_i - 3\,\frac{(\mathbf{r}_i\cdot\mathbf{s}_i)\mathbf{r}_i}{r_i^2}\right] \qquad (6\text{-}77b)$$

Since both $\mathbf{r}_i$ and $\mathbf{s}_i$ transform as vectors under rotations of all electronic coordinates, $\mathbf{H}_S$ will do so also and hence will have its matrix elements diagonal in J proportional to those of $\mathbf{J}$, as required.

Combining the orbital and spin parts, we have

$$\mathbf{H}_J = -2\beta \sum_i \frac{1}{r_i^3}\left[\mathbf{l}_i - \mathbf{s}_i + \frac{3(\mathbf{r}_i\cdot\mathbf{s}_i)\mathbf{r}_i}{r_i^2}\right] \qquad \blacktriangleright\ (6\text{-}78)$$

Specialization for single-electron outside closed shells. When there is one electron not in a filled subshell, the only noncanceling terms in (6- arise from it. We may also drop the distinction between **l** and **L**, example. Thus, (6-78) becomes

$$\mathbf{H}_J = -\frac{2\beta}{r^3}\left[\mathbf{L} - \mathbf{S} + \frac{3(\mathbf{r}\cdot\mathbf{S})\mathbf{r}}{r^2}\right] \tag{6-7}$$

To obtain a from (6-73b), we must evaluate $\mathbf{H}_J \cdot \mathbf{J}$. This is

$$\mathbf{H}_J \cdot \mathbf{J} = \frac{-2\beta}{r^3}\left[\mathbf{L} - \mathbf{S} + \frac{3(\mathbf{r}\cdot\mathbf{S})\mathbf{r}}{r^2}\right]\cdot(\mathbf{L}+\mathbf{S})$$

Multiplying this out, and noting that $\mathbf{r}\cdot\mathbf{L} = \mathbf{r}\cdot(\mathbf{r}\times\mathbf{p}) = 0$, we obtain

$$-\frac{2\beta}{r^3}\left[\mathbf{L}^2 - \mathbf{S}^2 + \frac{3(\mathbf{r}\cdot\mathbf{S})^2}{r^2}\right]$$

If we now expand the last term in cartesian coordinates and use the prop erties of $S = \frac{1}{2}$ spin matrices that $S_x^2 = S_y^2 = S_z^2 = S(S+1)/3 = \frac{1}{4}$ an that $S_iS_j = -S_jS_i$, we find that it gives $S(S+1)$, just canceling the secon term. Thus we obtain $\mathbf{H}_J \cdot \mathbf{J} = -2\beta\mathbf{L}^2/r^3$, and, from (6-73$b$),

$$a = 2\beta\frac{\mu_I}{I}\left\langle\frac{1}{r^3}\right\rangle_{\text{av}}\frac{L(L+1)}{J(J+1)} \tag{▶ 6-80}$$

In a hydrogenic atom, $\langle 1/r^3\rangle_{\text{av}}$ can be expressed as

$$\left\langle\frac{1}{r^3}\right\rangle_{\text{av}} = \frac{1}{a_0^3}\frac{Z^3}{n^3L(L+1)(L+\frac{1}{2})} \tag{6-81}$$

where $a_0 = \hbar^2/me^2$ is the first Bohr radius. This leads to an $\mathbf{H}_J$ of th order of 10^5 gauss for the lowest states of hydrogen, and the a value i

$$a_H = \frac{2\beta}{a_0^3}\left(\frac{\mu_I}{I}\right)\frac{Z^3}{n^3(L+\frac{1}{2})J(J+1)} \tag{6-82}$$

For atoms with an inner core of filled shells, (6-82) is not valid though it can be used for estimation if a suitable effective Z is inserted. In principle, one should simply insert $\langle 1/r^3\rangle_{\text{av}}$, as calculated from a Hartree-Fock radial function, into (6-80). In practice, such functions are not always available, nor are they very accurate. Hence, it is frequently more reliable to infer $\langle 1/r^3\rangle_{\text{av}}$ from the experimentally measured fine-structure splitting. As noted in (6-51),

$$\zeta = \langle\xi(r)\rangle_{\text{av}} = \frac{\hbar^2}{2m^2c^2}\left\langle\frac{1}{r}\frac{dU}{dr}\right\rangle_{\text{av}}$$

Thus, if we define a $Z_p(r)$ which reproduces the potential by

$$U(r) = \frac{-Z_p(r)e^2}{r}$$

then the field is reproduced by a function $Z_f(r)$ defined by

$$\frac{dU}{dr} = \frac{e^2}{r^2}\left[Z_p(r) - r\frac{dZ_p(r)}{dr}\right] \equiv \frac{Z_f(r)e^2}{r^2}$$

and

$$\zeta = \frac{\hbar^2}{2m^2c^2}\left\langle\frac{Z_f(r)e^2}{r^3}\right\rangle_{\text{av}} = 2\beta^2\left\langle\frac{Z_f(r)}{r^3}\right\rangle_{\text{av}} \tag{6-83}$$

We can now express a in terms of the fine-structure splitting between $J = L \pm \frac{1}{2}$, namely, $\delta = (L + \frac{1}{2})\zeta$, as follows

$$\frac{a}{\delta} = \frac{\mu_I}{I\beta}\frac{L(L+1)}{(L+\frac{1}{2})J(J+1)}\frac{1}{Z_i} \tag{6-84a}$$

where

$$Z_i = \frac{\langle Z_f(r)/r^3\rangle_{\text{av}}}{\langle 1/r^3\rangle_{\text{av}}} \tag{6-84b}$$

Since the $1/r^3$ weighting factor emphasizes the interior of the atom, Z_i is an "interior" effective Z value, which is known semiempirically and from approximate calculations to be of the order of $(Z - 4)$ for p electrons.[1] From the form of (6-84) we see clearly that hyperfine-structure splittings are smaller than fine-structure splittings by a factor of the order of $(\mu_I/\beta) \sim (m/M) \sim 10^{-3}$.

Actually, there are sizable relativistic corrections to the result (6-84) which may amount to a factor of 2 or so in the heavy atoms. These were treated by Breit and by Racah in the early days of the subject.[2] Such calculations have been reviewed extensively by Kopfermann.[3]

Calculation of *a* for *S*-states. In an S-state, $L = 0$, and $J = S$. In this case, (6-80) becomes indeterminate, since $\langle 1/r^3\rangle$ becomes infinite, whereas $L(L+1)$ goes to zero. In fact, if we consider only the terms treated above, $\mathbf{H}_J$ is actually zero. $\mathbf{H}_L$ is obviously zero, since $\mathbf{L} = 0$, and $\mathbf{H}_S$ [as given by (6-77*b*)] can be shown to be zero for the spherical distribution of spin density which exists in an S state. However, a closer scrutiny of the problem shows that, in addition to (6-77*b*), there is a so-called "contact" hyperfine interaction which arises whenever there is a nonzero density of electronic magnetization inside the nucleus itself. This interaction was first worked out by Fermi[1] in 1930, using the Dirac equation to handle the relativist quantum mechanics of an electron moving very near (or inside) the nucleu More recently, it has been pointed out[2] that the existence of this conta interaction can be understood completely classically by using ordinar magnetostatics. Because of the greater clarity and simplicity of the clas cal argument, we shall be content to restrict our attention to it.

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[1] S. Goudsmit, *Phys. Rev.*, **43**, 636 (1933); E. Fermi and E. Segre, *Z. Physik*, **82**, 729 (1933).

[2] G. Breit, *Phys. Rev.*, **38**, 463 (1931); G. Racah, *Z. Physik*, **71**, 431 (1931).

[3] H. Kopfermann, "Nuclear Moments," chap. III, Academic Press Inc., New York, 1958.

The simplest model for the nuclear-dipole moment would be a rotatin spherical shell of radius r_0 with uniform surface-charge density. Fro classical magnetostatics, this will produce a pure dipole field outside th shell and a uniform field inside the shell of magnitude

$$\mathbf{B}_{\text{in}} = \frac{2}{r_0^{\,3}}\boldsymbol{\mu} = \frac{8\pi}{3V}\boldsymbol{\mu}$$

where V is the volume of the nuclear sphere. The magnetic interactio energy of this shell with the electronic magnetic-moment density $\mathbf{M}(\mathbf{r})$ can be written as

$$E = -\int \mathbf{B}(\mathbf{r}) \cdot \mathbf{M}(\mathbf{r})\, d\tau$$

Since $\mathbf{M}(\mathbf{r})$ is spherically symmetric in an S state, the integral of the produc of $\mathbf{M}(\mathbf{r})$ with the dipole field outside r_0 vanishes by symmetry. This leave only the integral inside the nuclear sphere, namely,

$$E = -\frac{8\pi}{3V}\boldsymbol{\mu} \cdot \mathbf{M}(0) \cdot V$$

where $\mathbf{M}(0)$ is the density of electronic magnetization inside the nucleus, which can be assumed constant over such a small volume. Since $\mathbf{M}(0) = -g_s\beta \sum_i |\psi_i(0)|^2\, \mathbf{s}_i$, where $|\psi_i(0)|^2$ is the probability density of the ith electron at the nucleus, we see that we can write the contact interaction energy operator as

$$H_c = \frac{8\pi}{3} g_s\beta \sum_i \delta(\mathbf{r}_i)\mathbf{s}_i \cdot \boldsymbol{\mu} \qquad ▶ \text{(6-85)}$$

or, for the case of a single unpaired electron,

$$H_c = a_c \mathbf{I} \cdot \mathbf{S} \tag{6-86a}$$

with

$$a_c = \left(\frac{\mu_I}{I}\right) \frac{8\pi}{3} g_s\beta\, |\psi(0)|^2 \tag{6-86b}$$

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[1] E. Fermi, *Z. Physik*, **60**, 320 (1930).

[2] See, for example, R. A. Ferrell, *Am. J. Phys.*, **28**, 484 (1960). Although this reference is almost certainly not the first to present this viewpoint, it is one of the more accessible. We should point out that the contact term can also be derived along with the usual dipole interaction (6–77*b*) if one calculates the field of the spin dipole moment $\mathbf{M}_s$ as $\mathbf{B}_s = \text{curl}\, \mathbf{A}_s$, with $\mathbf{A}_s = c^{-1} \int \mathbf{j}_s(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|\, d\tau'$ and $\mathbf{j}_s = c$ curl $\mathbf{M}_s$. With proper attention to vector-analysis identities, this procedure leads to both the ordinary dipole interaction and the contact interaction. The central point is that $\nabla^2(1/r) = -4\pi\delta(r)$. Because of the more physical and less mathematical nature of the argument given in the text, we have given it preference here.

Since the size of the nuclear sphere has dropped out, we can immediately generalize this argument to an arbitrary spherically symmetric distribution of nuclear magnetism. Because of the spherical symmetry of the contacting electrons, only the spherical part of the nuclear moment contributes. Hence, the result (6-85) or (6-86) should be generally valid, as is in fact the case.

It is a curious fact that for hydrogen, $|\psi(0)|^2$ has such a value that the a calculated by this formula agrees exactly with the value obtained if L is set equal to zero in our previously derived formula (6-82) for a_H. This apparent accident has been clarified by Satten,[1] who has shown that (6-86) can be obtained directly from (6-80) by a limiting process in which L is formally allowed to approach zero continuously. Since $\langle 1/r^3\rangle \sim L^{-1}$, this leads to a finite value in (6-80) and detailed calculation shows that the numerical coefficient is exactly that found by Fermi. This consideration makes it reasonable that S-electron h.f.s. coupling is generally stronger than that of other electrons, as is implied by the factor $(L+\frac{1}{2})^{-1}$ in (6-82). Naturally this contact h.f.s. term arises only with S electrons because $\psi(0) = 0$ for $L > 0$.

Addition of external magnetic field. Any externally applied field $\mathbf{H}_0$ will interact with the magnetic moment both of the electrons and of the nucleus. Thus, the complete Hamiltonian is

$$H = a\mathbf{I}\cdot\mathbf{J} - \left(\frac{\mu_J}{J}\right)\mathbf{J}\cdot\mathbf{H}_0 - \left(\frac{\mu_I}{I}\right)\mathbf{I}\cdot\mathbf{H}_0 \tag{6-87}$$

where (μ_J/J) is usually written $-g_J\beta$, g_J being the Landé g factor of the electronic state as given in (6-65). As with the ordinary Zeeman effect, the solution is particularly simple in either the weak or the strong-field limit. In fact, we may directly transcribe the results of Sec. 6-10, with obvious changes in notation and allowance for the fact that neither (μ_J/J) nor (μ_I/I) has any universal value.

In the weak-field limit ($\mu_J\mathrm{H}_0 \ll a$), we take diagonal elements in an $|IJFM)$ representation and obtain

$$\begin{aligned} E(IJFM) = {} & \left(\frac{a}{2}\right)[F(F+1) - I(I+1) - J(J+1)] \\ & - \frac{M\mathrm{H}_0}{2F(F+1)}\left\{\left(\frac{\mu_J}{J}\right)[F(F+1) - I(I+1) + J(J+1)]\right. \\ & \left. + \left(\frac{\mu_I}{I}\right)[F(F+1) + I(I+1) - J(J+1)]\right\} \end{aligned} \tag{6-88}$$

This formula describes how the $(2F+1)$-fold degenerate levels split into $(2F+1)$ equally spaced sublevels, with separation increasing linearly with

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[1] R. A. Satten, unpublished.

H_0. Note that, since $\mu_I \sim (m/M)\mu_J$, the term in (μ_I/I) can be neglec except when very high accuracy is required. On the other hand, if t experiment is intended to measure μ_I from this term, an overall accur of a part per million is required to provide reasonable accuracy for μ_I.

In the strong-field, or Back-Goudsmit, limit, $\mu_J\mathsf{H} \gg a$, and the ΔF ± 1 off-diagonal elements of $\mathbf{J} \cdot \mathbf{H}_0$ destroy F as a useful zero-order quantu number. Instead, we choose a decoupled representation which diagonali

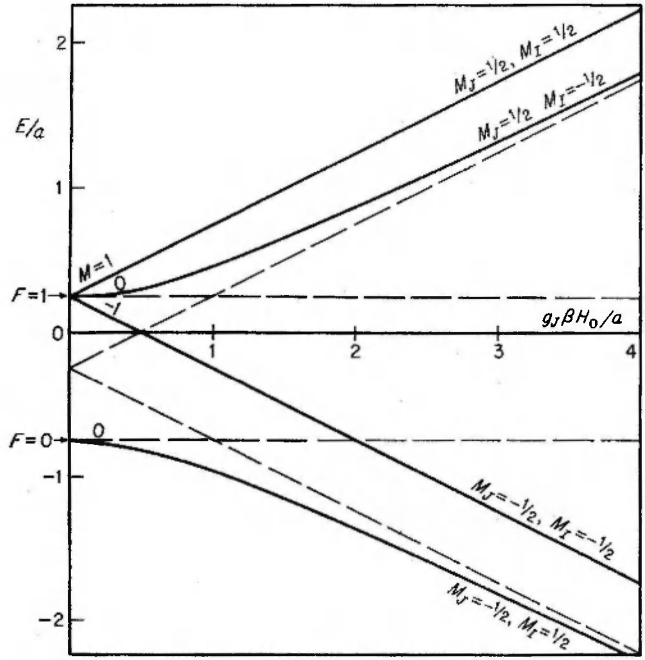

Fig. 6-4. *Application of Breit-Rabi formula for $I = J = \frac{1}{2}$.*

M_J and M_I, and hence the Zeeman energy, but leaves $\mathbf{I} \cdot \mathbf{J}$ partly off diagonal. The diagonal energy in the $|IJM_IM_J)$ representation forms the strong-field limit to the energy expression, namely,

$$E(IJM_IM_J) = aM_JM_I - \mathsf{H}_0\left[\left(\frac{\mu_J}{J}\right)M_J + \left(\frac{\mu_I}{I}\right)M_I\right] \qquad \text{(6-89)}$$

For intermediate field strengths, one must solve the secular equation more exactly, the effect of off-diagonal terms being included just as discussed in Sec. 6-10. In the simple case of $J = \frac{1}{2}$ and arbitrary I, the exact solution given there as Eq. (6-71) may be applied. In this connection, it is referred to as the *Breit-Rabi formula*[1] and is usually quoted in the form:

$$E(IJFM) = -\frac{\Delta W}{2(2I+1)} - \frac{\mu_I}{I}\mathsf{H}_0 M \pm \frac{\Delta W}{2}\left[1 + \frac{4Mx}{2I+1} + x^2\right]^{\frac{1}{2}} \qquad \blacktriangleright\ (6\text{-}90)$$

where $\Delta W = (a/2)(2I+1)$ is the field-free h.f.s. splitting and

$$x = [-(\mu_J/J) + (\mu_I/I)](\mathsf{H}_0/\Delta W)$$

is a dimensionless measure of the strength of the applied field. This formula plays a central role in the interpretation of atomic-beam experiments.

The results are sketched in Fig. 6-4 for the simplest case, namely, $I = J = \frac{1}{2}$, $F = 0, 1$. This applies to the ground state of atomic hydrogen, for example. Note that the $M = \pm 1$ levels diverge linearly at all fields because they are always pure states with $M_J = M_I = \pm\frac{1}{2}$, respectively. The two $M = 0$ levels, however, are composed of $M_J = -M_I = \pm\frac{1}{2}$ in a linear combination which depends on H_0. At $\mathsf{H}_0 = 0$, they are mixed equally, giving no resultant magnetic moment, and hence $(\partial E/\partial \mathsf{H}_0)_0 = 0$. As H_0 increases, the off-diagonal matrix elements between them change these proportions in such a way as to give the characteristic "repulsion" of two energy levels with the same group-theoretical symmetry.

In concluding this section, we might emphasize that, because typically $a \sim 10^{-3}\zeta$, the values of H_0 giving the Back-Goudsmit decoupling of F into I and J occur at a field of order 10^3 gauss, whereas the Paschen-Back decoupling of J into L and S occurs only for $\mathsf{H}_0 \sim 10^6$ gauss. Thus one does not usually need to treat the intermediate case of both decoupling simultaneously.

6-12 Electric Hyperfine Structure

The term in the energy which we seek here is the electric-quadrupole interaction. This has usually been deduced by elementary but tedious means. Instead of this, we shall take advantage of our development of Wigner and Racah coefficients to give a more elegant treatment of the electrostatic interaction between the nuclear and electronic charge. In our treatment we shall neglect any electronic charge which lies within the nuclear radius. As long as we consider only atoms, only S electrons penetrate the nucleus. Since they have a spherically symmetric distribution, they give no quadrupole coupling and so no error results from their omission. Under this assumption, we always have $r_< = r_n$ and $r_> = r_e$. Therefore the expansion of $|\mathbf{r}_n - \mathbf{r}_e|^{-1}$ in terms of the Legendre polynomials following (6-33) is simply

$$\frac{1}{r_{ne}} = \frac{1}{r_e}\sum_L \left(\frac{r_n}{r_e}\right)^L P_L(\cos\omega_{en}) \tag{6-91}$$

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[1] G. Breit and I. Rabi, *Phys. Rev.*, **38**, 2082 (1931).

where $\mathbf{r}_n$ and $\mathbf{r}_e$ are measured from the center of the nucleus to an ele of nuclear and electronic charge, respectively, and ω_{en} is the angle bet the directions ω_e and ω_n of $\mathbf{r}_e$ and $\mathbf{r}_n$. Introducing the spherical harm addition formula (6-34) and normalized spherical harmonics $Y_M{}^L$, we h

$$\frac{1}{r_{ne}} = \frac{1}{r_e}\sum_L \left(\frac{r_n}{r_e}\right)^L \left(\frac{4\pi}{2L+1}\right) \sum_{M=-L}^{L} (-1)^M Y_M{}^L(\omega_n)\, Y_{-M}{}^L(\omega_e) \qquad (6$$

We note that this interaction automatically breaks up into a sum of sc operators, each of which is the contraction of two irreducible tensor erators of rank L. We now examine the first few terms.

For $L = 0$, we have simply $1/r_e$, the ordinary Coulomb monopole te If we integrate this interaction over the nuclear- and electronic-charge d sities ρ_n and ρ_e, we find its contribution to the system energy to be

$$\left[\int \rho_n(r_n)\, d\tau_n\right] \cdot \left[\int \frac{\rho_e(r_e)\, d\tau_e}{r_e}\right] = [Ze] \cdot \int \frac{\rho_e(r_e)\, d\tau_e}{r_e} \qquad (6\text{-}$$

For $L = 1$, we have three terms which can be rearranged to correspo to the three cartesian components. The energy is the scalar product of t two vectors,

$$\left[\int \rho_n(r_n)\mathbf{r}_n\, d\tau_n\right] \cdot \left[\int \rho_e(r_e)\mathbf{r}_e/r_e{}^3\, d\tau_e\right] = -\,\boldsymbol{\mu}_e \cdot \mathbf{E} \qquad (6\text{-}9$$

where $\boldsymbol{\mu}_e$ is the nuclear electric-dipole moment and $\mathbf{E}$ is the electric field the nucleus produced by the electronic-charge cloud. This term vanish both because $\boldsymbol{\mu}_e = 0$ by parity conservation and because $\mathbf{E} = 0$, if t nucleus is in a position of equilibrium.

The term of interest is the quadrupole term, $L = 2$. This can be e pressed as the product of two cartesian dyadics $\frac{1}{6}\mathbf{Q} : \nabla\mathbf{E}$, but it is much simpl to leave it in its spherical form. The matrix elements which we desi can then be written down immediately by use of our equation (5-83), namel

$$\begin{aligned}(IJFM|\, H_Q\, |IJFM) &= \frac{4\pi}{5}\,(IJFM\,|\sum_M (-1)^M r_n{}^2 Y_M{}^2(\omega_n) r_e{}^{-3} Y_{-M}{}^2(\omega_e)|\, IJFM) \\ &= \frac{4\pi}{5}(-1)^{I+J-F}[(2I+1)(2J+1)]^{\frac{1}{2}}(I\|\, r_n{}^2 Y^2(\omega_n)\, \|I) \\ &\quad \times (J\, \|r_e{}^{-3} Y^2(\omega_e)\, \|J)\, W(IJIJ;\, F2) \qquad (6\text{-}95)\end{aligned}$$

The entire dependence on F is in the Racah coefficient. Upon using symmetry property of the W coefficient, $W(IJIJ;\, F2) = W(IIJJ;\, 2F)$. Thi second form is of a type given in the tables of Biedenharn, Blatt, and Rose.[1] It is

$$\begin{aligned}W(IIJJ;\, 2F) = 6(-1)^{F-I-J}&\left[\frac{(2J-2)!\,(2I-2)!}{(2J+3)!\,(2I+3)!}\right]^{\frac{1}{2}} \\ &\times [C(C+1) - \tfrac{4}{3}I(I+1)J(J+1)] \qquad (6\text{-}96)\end{aligned}$$

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[1] L. C. Biedenharn, J. M. Blatt, and M. E. Rose, *Revs. Modern Phys.*, **24**, 256 (1952).

where $C = F(F+1) - I(I+1) - J(J+1)$. Clearly C is the diagonal matrix element of $2\mathbf{I}\cdot\mathbf{J}$. Thus we have shown that the energy eigenvalues (for given I and J) are proportional to $[3(\mathbf{I}\cdot\mathbf{J})^2 + \frac{3}{2}(\mathbf{I}\cdot\mathbf{J}) - \mathbf{I}^2\mathbf{J}^2]$, the result usually obtained by the elementary methods.

Although the answer obtained above is complete in so far as the dependence on F is concerned, it is worthwhile giving some attention to clarifying the significance of the reduced matrix elements so that we have a detailed connection with the conventional results. That is, we wish to express $(I\| r_n^2 Y^2(\omega_n) \|I)$ in terms of the nuclear-quadrupole moment Q and $(J\| r_e^{-3} Y^2(\omega_e) \|J)$ in terms of the field-gradient coupling constant q_J. From its definition in the Wigner-Eckart theorem, we have

$$(I\| r^2 Y^2(\omega_n) \|I) = \frac{(I, M_I + \mu|\, r^2 Y_\mu^2(\omega_n)\, |IM_I)}{A^{I2I}_{M_I\mu}} \tag{6-97}$$

This ratio can be evaluated for any values of μ and M_I, but it is simplest to choose $\mu = 0$ and $M_I = I$. Then (from the tables in Condon and Shortley)

$$A^{I2I}_{I0} = \frac{3M_I^2 - I(I+1)}{[(2I-1)I(I+1)(2I+3)]^{\frac{1}{2}}} = \left[\frac{I(2I-1)}{(I+1)(2I+3)}\right]^{\frac{1}{2}} \tag{6-98}$$

Now, the nuclear-quadrupole moment Q is conventionally *defined* by

$$eQ = \int [\rho_n(r_n)]_{M_I=I}\,(3z_n^2 - r_n^2)\,d\tau_n = \left(\frac{16\pi}{5}\right)^{\frac{1}{2}} \int \rho(r_n) r_n^2 Y_0^2(\omega_n)\,d\tau_n \tag{6-99}$$

Q has the dimensions of area, and it is a measure of the elongation along z of the nuclear charge when the nuclear spin is aligned as nearly along the z axis as possible. The indicated integration is equivalent to taking the $|II)$ diagonal matrix element. Thus, combining our results, we have

$$eQ = (II|\left(\frac{16\pi}{5}\right)^{\frac{1}{2}} r_n^2 Y_0^2(\omega_n)\,|II) = \left[\frac{16\pi}{5}\,\frac{I(2I-1)}{(I+1)(2I+3)}\right]^{\frac{1}{2}} (I\| r_n^2 Y^2(\omega_n) \|I) \tag{6-100}$$

We note that $Q = 0$ for $I = 0$ or $I = \frac{1}{2}$. Thus a nucleus can have no quadrupole moment as defined here unless its spin exceeds $\frac{1}{2}$.

In a similar manner, the field-gradient parameter in the electronic state J is defined by

$$\begin{aligned} eq_J = \left(\frac{\partial^2 V}{\partial z^2}\right)_{r=0, M_J=J} &= \int [\rho_e(r_e)]_{M_J=J}\,\frac{3z_e^2 - r_e^2}{r_e^5}\,d\tau_e \\ &= \left[\frac{16\pi}{5}\,\frac{J(2J-1)}{(J+1)(2J+3)}\right]^{\frac{1}{2}} (J\| r_e^{-3} Y^2(\omega_e) \|J) \end{aligned} \tag{6-101}$$

From this, we note that q_J vanishes unless $J > \frac{1}{2}$. Thus quadrupole effects can be observed only if both I and J exceed $\frac{1}{2}$.

Finally, we use these relations to eliminate the reduced matrix elem in our energy expression (6-95), using q_J and Q as parameters ins After canceling common factors, we obtain

$$(IJFM|\, H_Q \,|IJFM) = \frac{e^2 q_J Q}{2I(2I-1)J(2J-1)} \{\tfrac{3}{4}C(C+1) - I(I+1)J(J+$$

▶ (6-1

with $C = F(F+1) - I(I+1) - J(J+1)$. This is the form in which result is usually quoted, though often with C written as $2\mathbf{I}\cdot\mathbf{J}$.

For simple molecular problems, one can work out the explicit depende of q_J on the rotational state and include it in the formula. We shall go into any derivations[1] at this point but shall simply quote the result the case in which the nucleus under consideration lies on the axis of sy metry of a symmetrical top molecule, i.e., one with two equal moments inertia. In this case

$$q_J = \frac{3K^2 - J(J+1)}{(J+1)(2J+3)} q_0 \qquad (6\text{-}1$$

where q_0 is computed with respect to the molecular symmetry axis (rath than with respect to an axis fixed in space) and K is the quantized com ponent of $\mathbf{J}$ along that axis. Note that $q_J \to q_0$ if $K = J \to \infty$, as mu be true classically in this limit. Also note that, in a linear molecule, must be perpendicular to the axis, giving $K = 0$. Hence in that cas $q_J = -Jq_0/(2J+3)$.

Returning to the atomic case, since I and J must exceed $\frac{1}{2}$ for quadrupol effects, there is always a magnetic-dipole interaction as well. Thus th total h.f.s. Hamiltonian will be

$$H_{hfs} = H_m + H_Q$$

Because of overall rotational invariance, however, F must be a good quan tum number even in this case. In fact, the energy levels are readily writte down by simply summing the contributions of H_m and H_Q to the diagon matrix element of H_{hfs} in an $|IJFM)$ representation. Thus

$$E(IJFM) = \frac{a}{2}C + \frac{e^2 q_J Q}{2I(2I-1)J(2J-1)} \{\tfrac{3}{4}C(C+1) - I(I+1)J(J+1)\} \qquad (6\text{-}104)$$

where again $C = 2\mathbf{I}\cdot\mathbf{J} = F(F+1) - I(I+1) - J(J+1)$.

If we now add a weak magnetic field, we can proceed exactly as before, since our zero-order eigenfunctions are unchanged. Thus we simply add to (6-104) the term in H_0 given in (6-88) to describe the linear Zeeman-effect region. In the other extreme, the strong-field region, we take $|IJM_IM_J)$ quantization and add to (6-89) the diagonal elements of H_Q in this representation. These are readily obtained from (6-95) by using the Wigner-Eckart theorem on the electronic and nuclear operators separately. Thus

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[1] See, for example, C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," chap. 6, McGraw-Hill Book Company, Inc., New York, 1955; N. F. Ramsey, "Nuclear Moments," p. 19, John Wiley & Sons, Inc., New York, 1953.

$$(IJM_IM_J|\, H_Q\, |IJM_IM_J) = \frac{4\pi}{5}(I\|\, r_n{}^2 Y^2(\omega_n)\, \|I)(J\|\, r_e{}^{-3} Y^2(\omega_e)\, \|J) A^{I2I}_{M_I0} A^{J2J}_{M_J0} \tag{6-105}$$

Using (6-100) and (6-101) to express the reduced matrix elements in terms of eQ and eq_J, and using the fact that

$$A^{I2I}_{M_I0} = \frac{3M_I{}^2 - I(I+1)}{[(2I-1)I(I+1)(2I+3)]^{\frac{1}{2}}}$$

(and similarly for $A^{J2J}_{M_J0}$), we find that

$$(IJM_IM_J|\, H_Q\, |IJM_IM_J) = \frac{e^2Qq_J}{4} \frac{[3M_I{}^2 - I(I+1)]}{I(2I-1)} \frac{[3M_J{}^2 - J(J+1)]}{J(2J-1)} \tag{6-106}$$

This is the term to be added to (6-89) to get the contribution of H_Q to the energy in the strong-field limit.

In the intermediate-field region, we need off-diagonal matrix elements as well. These are obtained by the same procedure used in (6-105), except that in the $(M_I + \mu, M_J - \mu|\, H_Q\, |M_IM_J)$ matrix element, we have a factor of $A^{I2I}_{M_I\mu} A^{J2J}_{M_J,-\mu}$. The formula in (6-105) is the specialization of this result for $\mu = 0$. Given all the matrix elements, perturbation theory or more exact procedures can be used to compute the energy levels.

Further refinements. Our treatment so far has indicated the main features in the calculation of hyperfine structure. However, to get very high accuracy a number of corrections must be considered. One arises because of the existence of $\Delta J = \pm 1$ matrix elements in H_m and of $\Delta J = \pm 1, \pm 2$ matrix elements in H_Q, in addition to the $\Delta J = 0$ elements which we have used above. These off-diagonal elements will be particularly important if the fine-structure interval is relatively small, rather than immense in comparison with h.f.s. energies. They can be calculated from generalizations of the procedures given above, but of course new parameters, such as $q_{JJ'}$, are introduced, which must be estimated theoretically if correction for these effects is to be made.

Another sort of correction, which fortunately does not change the form of the results but does interfere with a simple interpretation of the numerical values, is the so-called "Sternheimer[1] shielding" or "antishielding effect." Sternheimer has shown that the exterior field of a nuclear- pole moment produces a significant polarization of the core electron atom. This can have the effect of either increasing or decreasing the magnitude of e^2qQ from that obtained by considering only unper valence electrons as producing a field acting on the bare nucleus. corrections can be sizable and are hard to evaluate reliably. Thus lute values of Q are hard to obtain with confidence even though th perturbed electronic wavefunction may be reasonably well known.

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[1] R. M. Sternheimer, *Phys. Rev.*, **80**, 102 (1950); **84**, 244 (1951); **86**, 316 (1952); **95**, 736 (1954).

After making the small corrections for off-diagonal elements ment above, the field-free h.f.s. spectrum should be rigorously fitted by adjus of two parameters: a for the magnetic dipole and e^2qQ for the el quadrupole. If this is not possible, one is led to attribute the discrep to the effect of a nuclear-octupole moment, the next nonvanishing nu moment. Such moments have now been measured for several nuclei, the interaction cannot possibly be observed unless both I and J are $\frac{3}{2}$ or gr This can be seen in an elementary way by noting that, if either I or J is than $\frac{3}{2}$, there will be at most two energy-level differences to fit, and this certainly be done with two parameters. The same conclusion could, course, be reached by inspecting the Wigner coefficients. Although shall not carry the problem further here, extensive discussions of calculati including those with the higher nuclear moments, are available in the lit ture.[1]

EXERCISES

6-1 The wavefunction of a helium atom is reasonably approximated as product of two hydrogenic 1*s* functions $Ne^{-\alpha r}$, where α is a parameter to be dete mined by the variational principle and N is a normalizing constant. Find N, an then compute the potential experienced by one electron in the field of the nucl and the other electron. Show that it is given by

$$U(r) = -\frac{e^2}{r}\{1 + (1 + \alpha r)e^{-2\alpha r}\}$$

6-2 (*a*) Using the potential found in Exercise 6-1, calculate the total energy an electron with wavefunction $N'e^{-\alpha' r}$. (*b*) Set up an expression to find the valu of α' giving the lowest energy for given α. Then, set $\alpha = \alpha'$ as required by sym metry, solve for α in units of $(1/a_0)$, and find the corresponding binding energy a He 1*s* electron. Compare with the experimental ionization potential of 1.8 rydbergs. (*c*) Note that you get a different, and incorrect, answer, if you set $\alpha = \alpha'$ *before* applying the variational principle to the one-electron energy. Explain this discrepancy. (*d*) Calculate the total binding energy of the two-electron system with respect to the energy of separated particles. Note that this is *not* the value found in (*b*). Since the binding energy of an atom with $Z = 2$ with electron in a $1s$ orbital is rigorously 4 rydbergs, evaluate the binding energy second electron by subtracting the 4 rydbergs from the two-electron binding gy. Compare with the result of (*b*). The near equality of these results trates Koopmans' theorem[1], namely, that the ionization potential differs only cond order from the Hartree one-electron energy parameter. In fact, helium vides a very severe test of the theorem, since the removal of one electron makes largest change when it is removed from a two-electron system.

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[1] See, for example, C. Schwartz, *Phys. Rev.*, **105,** 173 (1957).

6-3 (*a*) Consider a lithium atom ($Z = 3$) with a $1s^2$ core and one valence ctron. As suggested by Exercises 6-1 and 6-2, assume that the core charge be roughly approximated by that of hydrogenic $1s$ functions, but with an ctive $(Z - s) = 2$, so that $\rho/e = (2a^3/\pi)e^{-2ar}$, with $a = 2/a_0$. Use Poisson's uation of electrostatics to calculate the potential as a function of r, and show t it is given by

$$U = \frac{-e^2}{r} - (Z - 1)\left(\frac{e^2}{r}\right)(1 + ar)e^{-2ar}$$

(*b*) From the potential found in (*a*), compute and plot $Z_p(r)$ and $Z_f(r)$, the effective nuclear charges for potential and field, as defined in conjunction with Eq. (6-83).

6-4 Approximate the excited-state $2p$ orbital for the neutral lithium atom of Exercise 6-3 by the expression

$$\psi_{2p}(r, \theta, \varphi) = Are^{-br}Y_l^m(\theta, \varphi)$$

where A is a normalizing constant and b is an adjustable parameter. Taking the potential found in Exercise 6-3*a*, find the best value of b by the variational method. (You will have to use successive approximations, but convergence is rapid.) For this best value, what is the binding energy of the $2p$ electron? (The experimental value is 0.260 rydberg.)

6-5 Using the potential and ψ_{2p} found in Exercises 6-3 and 6-4, calculate the spin-orbit parameter $\zeta(2p)$, and thence the splitting between the ${}^2P_{\frac{1}{2}}$ and ${}^2P_{\frac{3}{2}}$ states. (The experimental splitting is 0.34 cm^{-1}.)

6-6 Compute the value of $\langle 1/r^3 \rangle$ for ψ_{2p} as given in Exercise 6-4. From this value and the results of Exercise 6-5, compute Z_i as defined in (6-84*b*). [The usual procedure is actually the reverse—namely, one takes ζ from experiment, estimates Z_i, and then infers $\langle 1/r^3 \rangle$ for the interpretation of h.f.s. data.]

In Exercises 6-7 *to* 6-10 *consider the* nd^2 *configuration.*

6-7 By setting up an M_L, M_S table of determinants as in Table 6-1, work out the terms allowed by the exclusion principle. Note that the table need be set up only for $M_L \geqq 0$, $M_S \geqq 0$, since the rest follows from symmetry.

6-8 (*a*) Express the energies of these allowed terms in terms of diagonal matrix elements between determinantal functions. (Use Slater-sum-rule method.) (*b*) Reduce these in terms of the standard radial integrals $F_0(nd^2)$, $F_2(nd^2)$, $F_4(nd^2)$. (*c*) Find the condition which these F's must satisfy if the Hund rules for determining the ground term are to be satisfied.

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[1] *Physica*, **1**, 104 (1933).

6-9 (*a*) Work out the eigenfunctions of the $M_L = 3$, $M_S = 0$ states b ing to the ^1G and ^3F terms as linear combinations of the simple determ (*b*) Using the tables of Wigner coefficients, find the $M_J = 3$ eigenfunctions the $J = 3$ and $J = 4$ levels of the ^3F term, again as linear combinations of t determinants.

6-10 Find the spin-orbit coupling parameter $\zeta(LS)$ for all nd^2 L-S te terms of the parameter

$$\zeta(nd) = (nd|\,\xi(r)\,|nd) = \int_0^\infty R_{nl}^2(r)\xi(r)\,dr$$

where $\quad \psi(r, \theta, \varphi) = r^{-1}R_{nl}(r)Y_l^m(\theta, \varphi) \qquad$ and $\qquad \displaystyle\int_0^\infty R_{nl}^2(r)\,dr = 1$

6-11 Assume that one has three orthogonal orbital wavefunctions a, b, c, each occupied by one electron. This system will have a spin degenera $2^3 = 8$, because we can associate either α or β spin functions with each sp orbital. (*a*) Enumerate the possible determinantal states. (*b*) For the spin-free approximate Hamiltonian, eigenvalues of S_z and $\mathbf{S}^2$ are good repres tion labels. What eigenvalues of these operators occur in this exercise, and frequently does each appear? (*c*) Find orthonormal combinations of the ab determinants which diagonalize these spin operators. Note that your results not unique for any symmetries appearing more than once. In that case a se equation based on the Hamiltonian is required to obtain the proper eigenfunctio How large is the maximum secular problem remaining after applying the symmetry considerations?

6-12 If an atom is in a $2p^2\ {}^3P_0$ state, to which of the following states is electric-dipole transition allowed? Explain in each case. (*a*) $2p3d\ {}^3D_2$, $2s2p\ {}^3P_1$, (*c*) $2s3s\ {}^3S_1$, (*d*) $2s2p\ {}^1P_1$.

6-13 (*a*) Use second-order perturbation theory to compute the correctio to the low-field Zeeman-effect result (6-88). The off-diagonal matrix eleme of J_z and I_z in an $|IJFM)$ representation which you require can be obtained using (5-84) as in Exercise 5-11. (*b*) Show that, if you specialize your result $J = \frac{1}{2}$, it is in agreement with the exact Breit-Rabi result to terms in x^2.

6-14 Derive the contact hyperfine interaction (6-85) in addition to the usu hyperfine coupling of dipolar form by the method indicated in the footno preceding that equation.

REFERENCES

CONDON, E. U., and G. H. SHORTLEY: "The Theory of Atomic Spectra," chap 5–7, 16, Cambridge University Press, New York, 1951.

EYRING, H., J. WALTER, and G. E. KIMBALL: "Quantum Chemistry," chap. 9, Joh Wiley & Sons, Inc., New York, 1944.

HARTREE, D. R.: "The Calculation of Atomic Structures," John Wiley & Son Inc., New York, 1957.

KOPFERMANN, H.: "Nuclear Moments," chaps. 1, 3, Academic Press Inc., Ne York, 1958.

I, N. F., and I. N. SNEDDON: "Wave Mechanics and Its Applications," chaps. 5 and 6, Oxford University Press, New York, 1948.

ULING, L., and E. B. WILSON, JR.: "Introduction to Quantum Mechanics," chaps. 8 and 9, McGraw-Hill Book Company, Inc., New York, 1935.

MSEY, N. F.: "Nuclear Moments," chap. 2, John Wiley & Sons, Inc., New York, 1953.

ATER, J. C.: "Quantum Theory of Atomic Structure," vols. I and II, McGraw-Hill Book Company, Inc., New York, 1960.

7 MOLECULAR QUANTUM MECHANICS

7-1 Born-Oppenheimer Approximation

At the foundation of all quantum-mechanical treatments of molecular problems is the fact that the great disparity of electronic and nuclear masses allows the problems of nuclear and electronic motion largely to be separated. This was shown in 1927 by Born and Oppenheimer in their classic paper.[1] In this section we review the results of this treatment. We take as our total Hamiltonian

$$H = -\sum_{\alpha} \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^{\,2} - \sum_{i} \frac{\hbar^2}{2m} \nabla_i^{\,2} + V_{nn} + V_{ne} + V_{ee} \qquad (7\text{-}1)$$

where α runs over all the nuclei, i runs over the electrons, and the V's are potential energies depending on positions of nuclei (n) and electrons (e),

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[1] M. Born and R. Oppenheimer, *Ann. Physik*, **87**, 457 (1927).

Now, if the nuclei were "clamped" in position as if infinitely massive, the Hamiltonian would be simply

$$H_e = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + V_{ee} + V_{ne} + V_{nn} \tag{7-2}$$

and there would be electronic eigenfunctions $\psi_e(\mathbf{r}_i; \mathbf{R}_\alpha)$ which satisfy $H_e\psi_e = E_e\psi_e$. These electronic eigenfunctions and eigenvalues depend parametrically on $\mathbf{R}_\alpha$ because of the term V_{ne}. As long as we hold the nuclei clamped in place, we can consider the term V_{nn} as a simple additive constant in the Hamiltonian. This will have no effect on the ψ_e but will add directly to the eigenvalue E_e. We may now write the total Hamiltonian as

$$H = H_e + H_n = H_e - \sum_\alpha \frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 \tag{7-3}$$

What Born and Oppenheimer did was to show that, because (m/M_α) is so small, we can treat H_n as a small perturbation. The suitable expansion parameter turns out to be $\kappa = (m/M)^{\frac{1}{4}}$, where M is an average nuclear mass. Clearly, κ is typically of order 0.1. Born and Oppenheimer carried out a systematic expansion of the eigenfunctions and eigenvalues in powers of κ. If one considers only small displacements from an equilibrium configuration of nuclei, the terms linear in κ vanish in defining the equilibrium configuration, the quadratic terms give the vibrational energy, the cubic terms vanish, and the quartic terms give the rotational energy, and some corrections to the vibrational energy. It also turns out that one must carry the analysis through fourth order to determine properly the complete zero-order eigenfunction. This is natural, since the eigenfunction must include the rotational as well as vibrational and electronic parts. We shall not go through this lengthy, but rather straightforward, analysis. Rather, we shall merely confirm that the results are reasonable.

In the zero-order Born-Oppenheimer approximation to the eigenfunctions (which is all that one normally uses), one writes an approximate total eigenfunction of H as a simple product,

$$\psi = \psi_e\psi_n \tag{7-4}$$

where $\psi_e(\mathbf{r}_i; \mathbf{R}_\alpha)$ is the eigenfunction of H_e and $\psi_n(\mathbf{R}_\alpha)$ depends only on $\mathbf{R}_\alpha$. We now test this approximation by trying to satisfy the equation

$$H\psi = (H_e + H_n)\psi_e\psi_n = E\psi_e\psi_n \tag{7-5}$$

To carry out the indicated operations, we note that

$$\nabla_\alpha^2\psi_e\psi_n = \nabla_\alpha\cdot\nabla_\alpha\psi_e\psi_n = \psi_e\nabla_\alpha^2\psi_n + 2\nabla_\alpha\psi_e\cdot\nabla_\alpha\psi_n + \psi_n\nabla_\alpha^2\psi_e$$

and

$$\nabla_i^2\psi_e\psi_n = \psi_n\nabla_i^2\psi_e$$

since ψ_n is independent of $\mathbf{r}_i$ but ψ_e depends on $\mathbf{R}_\alpha$ parametrically. T we have

$$\begin{aligned} H\psi &= (H_e + H_n)\psi_e\psi_n \\ &= -\left\{\sum_\alpha \frac{\hbar^2}{2M_\alpha} \nabla_\alpha\psi_e \cdot \nabla_\alpha\psi_n + \sum_\alpha \frac{\hbar^2}{2M_\alpha} \psi_n \nabla_\alpha^2\psi_e\right\} - \psi_e \sum_\alpha \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2\psi_n \\ &\quad - \psi_n \sum_i \frac{\hbar^2}{2m} \nabla_i^2\psi_e + (V_{nn} + V_{ne} + V_{ee})\psi_e\psi_n \\ &= -\{\quad\} + \psi_n H_e \psi_e + \psi_e H_n \psi_n \\ &= -\{\quad\} + E_e(\mathbf{R}_\alpha)\psi_e\psi_n + \psi_e H_n \psi_n \qquad (7 \end{aligned}$$

Now, if we neglect the term in braces, we can set $H\psi = E\psi$, factor out since it is no longer operated on, and obtain

$$[H_n + E_e(\mathbf{R}_\alpha)]\psi_n = E\psi_n \qquad (7$$

This equation serves as the Schrödinger equation for ψ_n. It says sin that the nuclei move in an effective potential which is the electronic ene for the relevant state [including $V_{nn}(\mathbf{R}_\alpha)$], as a function of the internucl distances. This separation of the problem is physically very reasonab The light electrons orbit around so rapidly compared with the motion the heavy nuclei that we can approximately solve for their motion by co sidering the nuclei to be fixed. We then include the energy of this electron motion in the effective potential for the quasi-static nuclear motion.

To test the validity of the approximation, we now examine the size of t term in braces which we had to drop to obtain our simple results. Th term might be viewed as a perturbation H' which will admix other produ functions $\psi_e'\psi_n'$ in forming the true eigenfunction. So long as the mat elements of H' are small compared with the zero-order energy differenc the approximation will be good. We can check this by comparing th terms in braces in (7-6) with the nuclear kinetic energy term, the smalle term not in braces. The ratios of these terms are

$$\frac{\nabla_\alpha\psi_e \cdot \nabla_\alpha\psi_n}{\psi_e\nabla_\alpha^2\psi_n} \quad \text{and} \quad \frac{\psi_n\nabla_\alpha^2\psi_e}{\psi_e\nabla_\alpha^2\psi_n}$$

These ratios are small to the extent that ψ_e depends less rapidly on $\mathbf{R}_\alpha$ tha does ψ_n. Now, ψ_n goes rapidly to zero if $\mathbf{R}_\alpha$ is displaced by a distance o the order of the amplitude of the zero-point motion, whereas ψ_e is so ex tended that it changes significantly only when $\mathbf{R}_\alpha$ is displaced by a distanc of the order of internuclear distances. The ratio of zero-point amplitude t tronic extension is readily shown to be of order $\kappa = (m/M)^{\frac{1}{4}}$, by an ument based on the observation that in the harmonic-oscillator approximation the restoring force for a given displacement is of the same order for trons and nuclei but that the masses differ in the ratio m/M. Thus we that the neglected terms would enter only in higher-order terms in the pansion parameter κ. This justifies our neglect of them as our usual ating approximation. Serious errors arise only in symmetrical molecules, where some of the zero-order eigenfunctions are actually degenerate. Then these neglected terms are able to exert decisive influence in splitting the degeneracy and determining the symmetries of the actual eigenfunctions. However, because this complication introduces only a small secular equation, we shall defer discussion of such situations until specific examples occur in our systematic treatment. This systematic approach commences with a discussion of the methods of solving the "clamped-nuclei" electronic problem. The solutions of this will provide not only the electronic energy levels but also the effective potential for vibrational motion.

7-2 Simple Electronic Eigenfunctions

The simplest molecules are those with only two centers. Since these already introduce most of the effects which make the molecular problem differ from the atomic one, while remaining relatively simple to think about, we shall concentrate quite a bit of attention on them.

As soon as there is more than one center, we loose the spherical symmetry which played such a vital role in our atomic calculations. This destroys the usefulness of $\mathbf{L}^2$ and (except in linear molecules) L_z for factoring secular equations. Also, it makes the Hartree-Fock equations, which apply just as well in principle, hopeless to solve rigorously, because our unknown eigenfunctions can no longer be expressed in terms of a single variable, $|r|$, as in the atomic case.

Our best hope in general is to set up a series of orthonormal orbitals having the symmetry of whatever molecule we are dealing with, calculate matrix elements of H_e between them, and solve the secular equation. This will give a set of *molecular orbitals* (MO's), which are then used somewhat as the atomic orbitals were used to build up atomic configurations. For this procedure to be practical, the starting functions (*symmetry orbitals*) must be well chosen to speed convergence. This precludes using atomic functions about one center but suggests the use of *linear combinations* of *atomic orbitals* (LCAO's) centered on the various nuclei. Such LCAO MO's form the basis for a large share of current calculations on molecular structure. Another possible method for diatomic molecules is the use of MO's which really have the two centers "built in." The exact eigenfunctions for $H_2{}^+$, which can be found by separation of variables in elliptic coordinates, are the prototypes for such functions, just as the H atomic eigenfunctions a foundation for approximations suitable for atomic problems.

Hydrogen-molecule ion, H_2^+. Since an exact solution[1] is available f hydrogen-molecule ion, it is valuable as a practice problem for tryin approximation methods which can be carried over to the less simple cules.

The simplest approximation to the ground state which we could se would be an MOLCAO

$$\psi = c_a a + c_b b \qquad ($$

where a and b are ordinary hydrogen 1s wavefunctions centered on pro a and b, the two centers of the problem. Symmetry requires that the

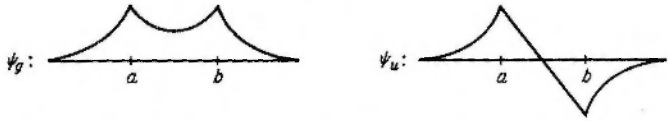

Fig. 7-1. *Even and odd molecular orbitals for the hydrogen-molecule ion,* H_2^+.

centers are equivalent. Therefore $|c_a| = |c_b|$, and $c_b = \pm c_a$. We must a little careful of normalization, because the functions a and b are orthogonal. The normalization requirement is

$$1 = \int \psi^* \psi \, d\tau = \int (c_a^* a^* \pm c_a^* b^*)(c_a a \pm c_a b) \, d\tau$$

$$= 2\,|c_a|^2 \pm 2\,|c_a|^2 \int a^* b \, d\tau \qquad (7\text{-}$$

since a and b are normalized and real. The integral

$$S_{ab} = \int a^* b \, d\tau \qquad (7\text{-}1$$

is called the *overlap integral* between the orbitals a and b. It is a measu of the degree of nonorthogonality. We can solve the normalization equati for $|c_a|$ and obtain the following two approximate molecular orbital taking c_a to be real for simplicity:

$$\psi_g = \frac{1}{\sqrt{2}\sqrt{1 + S_{ab}}} (a + b) \qquad \psi_u = \frac{1}{\sqrt{2}\sqrt{1 - S_{ab}}} (a - b) \qquad (7\text{-}11$$

Of these, ψ_g is obviously even on inversion through the midpoint of a an b, whereas ψ_u is odd. The qualitative forms of these wavefunctions a indicated in Fig. 7-1. Clearly these two wavefunctions will have differe ergies, ψ_g lying below ψ_u. The odd function, ψ_u, would appear to have ore energy for two reasons: (1) There is less charge in the central region, hich enjoys the attractive potential of both nuclei and correspondingly ore on the ends, where it feels only one nucleus. (2) The odd function as an extra node, and hence more kinetic energy associated with slope of e wavefunction. Although argument 2 has a certain heuristic appeal and often quoted, it cannot really be valid, because it is inconsistent with he virial theorem.[1] For the equilibrium nuclear configuration and for the xact eigenfunction, this theorem requires that the kinetic energy be exactly half the magnitude of the (negative) potential energy. Accordingly, the kinetic energy must cancel half the binding energy, and for maximum binding there will be a *maximum* kinetic energy. Thus, in fact, argument 1 must be relied on to account for the difference in energy of the two functions.

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[1] E. Teller, *Z. Physik*, **61**, 458 (1930); D. Bates, K. Ledsham, and A. L. Stewart, *Phi Trans. Roy. Soc.* (*London*), **246**, 215 (1953).

If the binding energy of ψ_g is computed as a function of internuclear distance $R_{ab} - R$, one finds a curve of the sort shown in Fig. 7-2. The

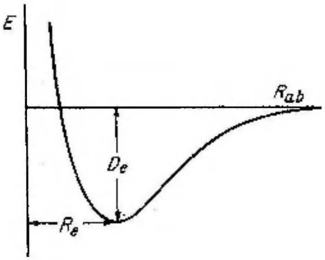

Fig. 7-2. *Dependence of molecular binding on internuclear distance.*

maximum binding (lowest energy) occurs at $R_e - 1.32$ A, where the binding energy D_e is 1.76 ev. Since the correct values, as found by experiment or from the exact solution, are $R_e = 1.06$ A and $D_e = 2.79$ ev, this leaves much room for improvement. One very simple but effective improvement[2] is to introduce an effective nuclear charge $Z'e$ into the hydrogenic functions. This allows adjustment of the radial scale of the atomic orbitals for each value of internuclear distance R. In this way one obtains the proper value $R_e = 1.06$ A and improves D_e to 2.25 ev, cutting the error in half. At R_e, $Z' = 1.228$, which lies between the values corresponding to counting one and both hydrogen nuclei, as might be expected. If one further modifies the atomic orbitals by polarizing them along the axis (by adding some p_σ character to the s functions), the binding energy can be improved to 2.71 ev. Finally, a simple analytic variation function, due to James,[3] can be set up in elliptical coordinates, namely,

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[1] For a discussion of the implications of the virial theorem in quantum mechanics, see P. O. Löwdin, *J. Mol. Spectroscopy*, **3**, 46 (1959).

[2] B. N. Finkelstein and G. E. Horowitz, *Z. Physik*, **48**, 118 (1928).

[3] H. M. James, *J. Chem. Phys.*, **3**, 7 (1935).

$$\psi = e^{-\delta\mu}(1 + c\nu^2)$$

where the elliptic coordinates are defined by $\mu = (r_a + r_b)/R_{ab}$ and $(r_a - r_b)/R_{ab}$. This function gives 2.772 ev, which is really quite near true value. This list of results should provide an idea of the accur which results from various types of approximations. Further details be found in various texts[1] as well as in the original literature.

7-3 Irreducible Representations for Linear Molecules

Homonuclear diatomic molecules $D_{\infty h}$. The notation D_∞ means th rotations C_φ through all possible angles φ about the symmetry (z) axis symmetry operations and that twofold rotations C_2' can be made about axis in the bisecting plane perpendicular to the z axis. The subscript implies the existence of the horizontal (xy) reflection plane with associat reflection σ_h. Combining this reflection with a 180° rotation about z giv the inversion i. Combining i with a C_2' gives a reflection in a vertical plan σ_v, which is usually preferred for symmetry classification. The irreducib representations and states are labeled in a way which indicates the tran formation properties under C_φ, i, and (for Σ states) σ_v. The charact table is given here, in slightly different form from that given in the Append

$D_{\infty h}$	E	$2C_\varphi$	σ_v	i	$2iC_\varphi$	$i\sigma_v = C'$
Σ_g^+	1	1	1	1	1	1
Σ_u^+	1	1	1	-1	-1	-1
Σ_g^-	1	1	-1	1	1	-1
Σ_u^-	1	1	-1	-1	-1	1
Π_g	2	$2\cos\varphi$	0	2	$2\cos\varphi$	0
Π_u	2	$2\cos\varphi$	0	-2	$-2\cos\varphi$	0
Δ_g	2	$2\cos 2\varphi$	0	2	$2\cos 2\varphi$	0
Δ_u	2	$2\cos 2\varphi$	0	-2	$-2\cos 2\varphi$	0
. . .	. . .	. . .	. . .	. . .	. . .	. . .

The primary quantum number in the representation label is $|L_z| = |\Lambda$ This is indicated by a Greek capital letter in analogy with the atomic schem ($S, P, D, \ldots$). Thus we have Σ, Π, Δ, . . . for $|\Lambda| = 0, 1, 2, \ldots$. Sma letters ($\sigma, \pi, \delta, \ldots$) are used if one is classifying a single electron state, aga in analogy with the atomic case. Except for Σ states, which must be nondegenerate, all these states are doubly degenerate since the two senses of rotation have the same energy. The basis functions transform like $e^{i\Lambda\varphi} = e^{\pm i|\Lambda|\varphi}$ under rotations. The character under C_φ for all representations follows immediately from this knowledge. The inversion character merely depends on the label, g or u, and the number of functions in the basis set. The $\pm$ label on the Σ states tells the character under σ_v, that is, whether or not the wavefunction changes sign when reflected in a plane through the internuclear axis. We note that the characters of all the two-dimensional representations under σ_v are zero. This follows from the fact that

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[1] See, for example, H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry chap. XI, John Wiley & Sons, Inc., New York, 1944; and L. Pauling and E. B. Wilson, Jr "Introduction to Quantum Mechanics," chap. XII, McGraw-Hill Book Company, Inc New York, 1935.

$$e^{\pm i|\Lambda|\varphi} \sim (x \pm iy)^{|\Lambda|}$$

A σ_v reflection takes y into $-y$, thus interchanging the basis functions, giving a traceless matrix representation. The characters under iC_φ and $i\sigma_v = C_2$ follow from the characters under C_φ and σ_v since i has a diagonal matrix representation.

These group-theoretical quantum numbers do not completely specify a state. We must give other information, equivalent to the configuration description in the atomic case, which specifies the nature of all occupied states, including principal quantum numbers as well as symmetry. The two conventional ways of specifying a one-electron state consist in giving the appropriate atomic quantum numbers in the limits (1) separated atoms and (2) united atom. For example, the $H_2{}^+$ ground state, ψ_g, would be labeled (1) $\sigma_g 1s$ or (2) $1s\sigma_g$. On the other hand, the ψ_u excited state would be labeled (1) $\sigma_u 1s$ or (2) $2p\sigma_u$. Note that the group-theoretical labels based on absolute symmetry considerations always are the same in either limiting description. In the united-atom scheme, ψ_u is called $2p\sigma_u$ because, as the two centers approach close together as if to form a united atom, the molecular orbital has the symmetry of an atomic p_z orbital about the midpoint.

Since it is relatively easy to estimate the order and position of the energy levels in the two limiting cases $R_{ab} \to 0$ and ∞, we can gain a qualitative picture of the energy-level structure at intermediate values of R_{ab} by setting up a *correlation diagram*. This correlation is based on the "no-crossing" rule on energy levels belonging to the same irreducible representation. A few of the lower levels are indicated in Fig. 7-3.

Examples. H_2 ■ Here we have only two electrons; so both can occupy the lowest σ_g orbital with spins opposed. Then $\Lambda = \sum_i \lambda_i = 0$, and we must have a Σ state. Since all orbitals are even under inversion and reflection, the state is $(\sigma_g 1s)^2$, ${}^1\Sigma_g{}^+$.

Li_2 ■ The six electrons fill the three lowest levels on the diagram (Fig. 7-3). By simple arguments, this gives a state $(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2$, ${}^1\Sigma_g{}^+$.

N$_2$ ■ (14 electrons). Assuming that the order of the levels at end is reliable, we still can make an unambiguous assignment usin correlation diagram alone. Experiment confirms that in fact the gro state is $(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4$. Again, the completely f "shells" lead to a $^1\Sigma_g^+$ state. Note that the $\pi_u 2p$ level holds four electr rather than two, because of the existence of $\Lambda = \pm 1$ degeneracy in add to the spin degeneracy.

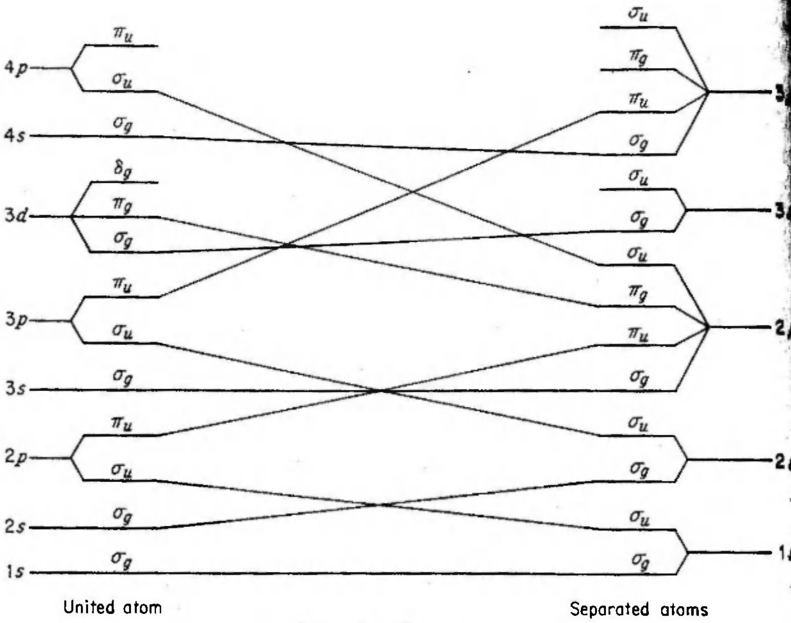
4p
4s
3d
3p
3s
2p
2s
1s
π_u
σ_u
σ_g
δ_g
π_g
σ_g
π_u
σ_u
σ_g
π_u
σ_u
σ_g
σ_g
σ_u
π_g
π_u
σ_g
σ_u
σ_g
σ_u
π_g
π_u
σ_g
σ_u
σ_g
σ_u
σ_g
3
3
2
2
1
United atom
Separated atoms
Increasing r_{ab} →

Fig. 7-3. *Correlation diagram for homonuclear diatomic molecules.*

O$_2$ ■ (16 electrons). If we add two more electrons to the N$_2$ fille shells, they go in as $(\pi_g 2p)^2$. This leaves an unfilled shell, since there room for four $\pi_g 2p$ electrons. Now Hund's rule has a chance to work, an indeed the ground state has the two spins parallel and thus orbits necessaril opposed. This leads to $\Lambda = 0$, but $S = 1$. It is a gerade state becau we are adding π_g electrons. But it is − under reflection because reflectio interchanges the two orbitals, which changes the sign of the antisymmetr electronic wavefunctions. Thus the ground state of O$_2$ is a $^3\Sigma_g^-$ stat From the same configuration we can also form $^1\Sigma_g^+$ and $^1\Delta_g$ excited state These three states enter into the most prominent atmospheric absorptio bands of O$_2$.

Heteronuclear diatomic molecules $C_{\infty v}$. In this case, we no longer have a center of symmetry, and hence we loose the parity quantum number. The symmetry group contains only C_φ and σ_v. The character table is

$C_{\infty v}$	E	$2C_\varphi$	σ_v
Σ^+	1	1	1
Σ^-	1	1	−1
Π	2	$2 \cos \varphi$	0
Δ	2	$2 \cos 2\varphi$	0
...	...	...	...

As can be seen by employing the arguments used for $D_{\infty h}$. Since the two atoms are now inequivalent, the correlation diagram is heavily modified at the separated-atom end, which now has twice as many distinct levels, each having half the degeneracy it had before.[1] The molecular orbitals in this case completely lose their inversion symmetry, and in general the low-lying orbitals have more charge attracted to the center with higher Z.

7-4 The Hydrogen Molecule

Since this is the simplest multielectron molecule, we shall look at it in some detail to illustrate and compare various methods. Regardless of the method, the Hamiltonian operator is the same and can be written

$$H = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \frac{1}{R_{a1}} - \frac{1}{R_{a2}} - \frac{1}{R_{b1}} - \frac{1}{R_{b2}} + \frac{1}{r_{12}} + \frac{1}{R_{ab}} \tag{7-12}$$

In this, we have shifted into *atomic units,* in which length is measured in units of the Bohr radius a_0, energy in units of 2 rydbergs or e^2/a_0, charge in

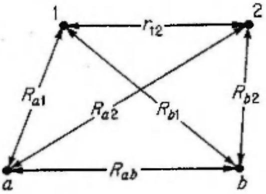

Fig. 7-4. *Geometry of* H_2 *molecule.*

units of e, mass in units of m, and angular momentum in units of $\hbar$. As indicated in Fig. 7-4, R_{a1} is the distance from nucleus a to electron 1, etc. An exact solution for eigenvalues and eigenfunctions of this Hamiltonian is no longer possible because of the r_{12}^{-1} interaction term. Therefore we shall examine several approximation schemes.

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[1] See Eyring, Walter, and Kimball, *op. cit.*, p. 210.

7-5 Molecular Orbitals

In this approximation to H_2, we describe the ${}^1\Sigma_g{}^+$ ground state of the by putting both electrons in the lowest or $(\sigma_g 1s)$ MOLCAO. The function is then given by

$$\psi = N[a(1) + b(1)][a(2) + b(2)]\,\frac{[\alpha(1)\beta(2) - \beta(1)\alpha(2)]}{\sqrt{2}}$$

N is a normalizing factor, and, as in Sec. 7-2, $a(1)$ is a hydrogenic $1s$ fun about nucleus a, having the explicit form $\pi^{-\frac{1}{2}}e^{-R_{a1}}$ in atomic units. last factor is the antisymmetric spin function corresponding to a singlet This provides the overall antisymmetry required by the Pauli prin as will be discussed later in more detail. If the energy is calculated this ψ, we find the maximum binding energy $D_e = 2.65$ ev occurrin $R_{ab} = R_e = 1.6a_0$. The experimental values are $D_e = 4.72$ ev and $1.40a_0$. In seeking the origin of this error of about 2 ev in the bin energy, we should recall that in $H_2{}^+$ the simple MO ground state fell ab 1 ev short of the correct value. This error was eliminated by adjusting radial scale and introducing polarization terms which threw charge into desirable region between the two nuclei, where it was bound by the attract of both. Coulson[1] carried out a similar calculation for H_2 in which determined a five-term approximation to the Hartree-Fock solution for "best" σ_g molecular orbitals. With these MO's he increased the calcula binding energy to about 3.6 ev, or halfway to the correct value. The maining error must lie largely in the fact that there is no interelectron correlation in the MO wavefunction. To illustrate this, let us return the simple LCAO MO's of Eq. (7-13) and expand the spatial part of th wavefunction to see what it is saying about the electrons. We find

$$\psi \sim a(1)a(2) + b(1)b(2) + a(1)b(2) + b(1)a(2)$$

From this, we note immediately that *ionic states*, in which both electron are on one center [such as $a(1)\,a(2)$], are given equal weight with the *covalen* ones [such as $a(1)b(2)$], in which there is one electron on each center. Sinc it takes more energy to remove an electron from one center than we gai by adding it as a *second* electron to the other center, these ionic states ar expected to be energetically less favorable. Therefore for best results the should appear in ψ with less weight, if at all.

We can make this improvement in several ways. The simplest is simply to drop the offending ionic terms. This leads to the *Heitler-London method*, which gives complete interatomic correlation. That is, if electron 1 is on nucleus a, then 2 is surely on b. This obviously will give the correct answers

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[1] C. A. Coulson, *Proc. Cambridge Phil. Soc.*, **34**, 204 (1938).

[2] W. Heitler and F. London, *Z. Physik*, **44**, 455 (1927).

$R_{ab} \to \infty$, whereas our simple MO picture would become hopelessly bad that limit. At the point of maximum binding, the Heitler-London hod yields $R_e = 1.64a_0$ and $D_e = 3.14$ ev, which is in better agreement h experiment by about 0.5 ev than the simple MO method. By introing a radial scale factor and polarization terms into the functions a and as described in connection with H_2^+, the computed binding energy can increased to 4.02 ev, again about 0.5 ev better than the "best" MO value.

We can do a slightly better job if the ionic states are not just thrown out t rather are reduced to the optimum degree by the variational method. is a useful illustration to view this as a simple example of *configuration teraction* within the MO picture. The only configurations which can mix n are those with the same overall group-theoretical symmetry, namely, $^1\Sigma_g^+$. The only other configuration of MO's made of $1s$ AO's having this symetry is $(\sigma_u 1s)^2$. In our same approximation, the wavefunction of this inglet state is

$$\psi' = N'[a(1) - b(1)][a(2) - b(2)] \frac{[\alpha(1)\beta(2) - \beta(1)\alpha(2)]}{\sqrt{2}} \tag{7-14}$$

Looking at the spatial part only, we find

$$\psi' \sim a(1)a(2) + b(1)b(2) - a(1)b(2) - b(1)a(2)$$

We note that the ionic terms and covalent terms enter ψ' with opposite sign, whereas in the $(\sigma_g 1s)^2$ configuration they entered with the same sign. Therefore, if we superpose the configurations to form a new function Φ given by

$$\Phi = c\psi + c'\psi' \tag{7-15}$$

and vary c and c' for minimum energy, we are in effect finding the optimum admixture of ionic states. When carried out, this variational problem is identical with solving the 2×2 secular equation between ψ and ψ'. It turns out that at R_e the optimum admixture of ionic states is only a few per cent. Thus the Heitler-London approximation is close to correct in this case. The relation among the various approximations has been considered particularly carefully by Slater[1] and by Coulson and Fischer.[2]

We might summarize our conclusions by stating that, of the 2-ev error in the simple MOLCAO ground state of H_2, about 1 ev is eliminated by going to MO's which give a more favorable one-electron potential energy by shifting charge into the internuclear region and another $\frac{1}{2}$ ev can be eliminated by introducing a simple type of correlation into the wavefunction. Since the Heitler-London method starts with this correlation in, the starting error is only 1.5 ev in the simple H-L method. This error can be reduc by the same 1 ev as with the MO's by choice of better atomic functio which shift charge into the favorable region.[1]

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[1] J. C. Slater, *Phys. Rev.*, **35**, 509 (1930), **41**, 255 (1932); *Tech. Rept.* 3, Solid State and Molecular Theory Group, MIT, 1953; "Quantum Theory of Molecules and Solids," vol. I, McGraw-Hill Book Company, Inc., New York, 1963.

[2] C. A. Coulson and I. Fischer, *Phil. Mag.*, **40**, 386 (1949).

So far we have followed the traditional practice for simple proble of writing ψ as a product of a space function times a spin function. Th technique becomes much less convenient when we have to deal with mo than two electrons. Therefore, let us work out the connection betwe these forms and the determinantal technique developed for the aton problem, which can handle any number of electrons.

A simple example is our MO ground state. There we have the dete minant

$$\psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_g(1)\alpha(1) & \sigma_g(2)\alpha(2) \\ \sigma_g(1)\beta(1) & \sigma_g(2)\beta(2) \end{vmatrix} \qquad \text{(7-1}$$

since both spin states of the $\sigma_g 1s$ orbital are (singly) occupied. The prop erties of determinants allow us to factor out factors common to all element of a column. This gives

$$\psi = \sigma_g(1)\sigma_g(2) \cdot \frac{1}{\sqrt{2}} \begin{vmatrix} \alpha(1) & \alpha(2) \\ \beta(1) & \beta(2) \end{vmatrix}$$

or, upon inserting our MOLCAO approximation for σ_g, we have

$$\psi = \frac{[a(1) + b(1)]}{[2(1 + S)]^{\frac{1}{2}}} \cdot \frac{[a(2) + b(2)]}{[2(1 + S)]^{\frac{1}{2}}} \frac{1}{\sqrt{2}} \begin{vmatrix} \alpha(1) & \alpha(2) \\ \beta(1) & \beta(2) \end{vmatrix} \qquad \text{(7-17}$$

Expansion of the determinant yields the spin function

$$[\alpha(1)\beta(2) - \beta(1)\alpha(2)]/\sqrt{2}$$

which we stated above in (7-13).

A more illuminating example is found by considering the $\sigma_g\sigma_u$ con- figuration. Since the electrons are not equivalent here, the spins can b parallel, forming a triplet state. Let us consider the $M_s = 1$ state, in which both electrons must be in the spin state α. We may factor out the common spin functions and normalizing factors from each column, as follows,

$$\psi(^3\Sigma_u{}^+, M_s = 1) = \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_g(1)\alpha(1) & \sigma_g(2)\alpha(2) \\ \sigma_u(1)\alpha(1) & \sigma_u(2)\alpha(2) \end{vmatrix}$$

$$= \frac{\alpha(1)\alpha(2)}{2^{\frac{3}{2}}(1 - S^2)^{\frac{1}{2}}} \begin{vmatrix} a(1) + b(1) & a(2) + b(2) \\ a(1) - b(1) & a(2) - b(2) \end{vmatrix}$$

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[1] The author is indebted to Dr. V. Heine for his illuminating remarks on this subject.

Where again we have used the simple LCAO approximation to both MO's. Expanding the determinant, and collecting terms, we find

$$\psi(^3\Sigma_u{}^+, M_s = 1) = \frac{b(1)a(2) - a(1)b(2)}{[2(1 - S^2)]^{\frac{1}{2}}}\,\alpha(1)\alpha(2) \tag{7-18}$$

From this we can obtain the states with $M_s = 0, -1$ by operating with S_-. They are unchanged except that the spin functions are

$$[\alpha(1)\beta(2) + \beta(1)\alpha(2)]/\sqrt{2}$$

and $\beta(1)\beta(2)$, respectively. We note that in all three cases these spin functions are symmetric under interchange of electrons 1 and 2, whereas the space function is antisymmetric. The resulting overall antisymmetry is an automatic consequence of using a determinantal form. We also note that the space function includes no ionic states. Therefore the MO and H-L methods are completely equivalent for this $^3\Sigma_u$ state.

If we had considered the $M_S = 0$ state of this $\sigma_g\sigma_u$ configuration, we could have written down the two determinants $(\sigma_g{}^+\sigma_u{}^-)$ and $(\sigma_g{}^-\sigma_u{}^+)$. We could then have diagonalized $\mathbf{S}^2$ between these two, finding that the linear combinations $[(\sigma_g{}^+\sigma_u{}^-) \pm (\sigma_g{}^-\sigma_u{}^+)]/\sqrt{2}$ corresponded to the singlet and triplet states. The triplet state would have agreed with that found in the previous paragraph. The other combination is

$$\psi(^1\Sigma_u{}^+) = \frac{a(1)a(2) - b(1)b(2)}{[2(1 - S^2)]^{\frac{1}{2}}}\,\frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}} \tag{7-19}$$

We note that this $^1\Sigma_u$ state is composed purely of ionic states. Hence, it will have a higher energy than $^3\Sigma_u$ states formed from the same configuration. This illustrates the fact that the Hund rule, that the state of maximum spin lies lowest, applies to molecules as well as to atoms—provided that it is possible to form a state with $S \neq 0$ from the prescribed configuration of occupied orbitals. The basic mechanism of the energy lowering is the same as in the atomic case: the antisymmetry correlates the two electrons with parallel spin so as to keep them away from each other by keeping them on different atoms. The $^3\Sigma_u$ state will still lie *above* the $^1\Sigma_g$ ground state, however, because of the excitation energy required to raise one electron from the $\sigma_g 1s$ orbital to the $\sigma_u 1s$ orbital. This does not violate the Hund rule, of course, because the rule holds only for comparisons of states formed from the same configuration of occupied one-electron orbitals.

7-6 Heitler-London Method

Although we have described the H-L method above as being a special simplified improvement of the molecular orbital method, it was in fact introduced on its own merits by Heitler and London and it continues to serve as the basis for many calculations. Therefore we now give it some de critical examination, paying particular attention to points which m cause confusion in its interpretation.

The H-L approximations to the $^1\Sigma_g$ and $^3\Sigma_u$ states of H_2 are

$$\psi(^1\Sigma_g) = N[a(1)b(2) + b(1)a(2)] \quad (7$$

$$\psi(^3\Sigma_u) = N'[a(1)b(2) - b(1)a(2)] \quad (7$$

These spatial functions are written down directly from a consideratio the equivalence of the two electrons and from the assumption that correl effects will prevent both electrons from being on the same center at the time. The spin functions do not enter naturally, as with the determin method, but are handled separately. This causes some difficulty in extension of the method of many-electron systems.

The main conceptual difficulties arise from the fact that, unlike ou and σ_u MO's, the basic functions here are not orthogonal. For exam

$$\iint [a(1)b(2)][b(1)a(2)]\, d\tau_1\, d\tau_2 = \left[\int a(1)b(1)\, d\tau_1\right]^2 = S_{ab}{}^2 \equiv S^2 \quad (7$$

Although some writers tend to throw away these overlap integrals when t get in the way, they are *not* small. Rather, they are often of order 0.3, a as we shall see, they are essential for the success of the method in its u form.

To make this point more precise, we consider in detail the energy of $^1\Sigma$ and $^3\Sigma$ states of H_2 in the H-L approximation. This is

$$\begin{aligned} E &= \iint \psi^* H \psi\, d\tau_1\, d\tau_2 \\ &= N^2 \iint [a(1)b(2) \pm b(1)a(2)] H [a(1)b(2) \pm b(1)a(2)]\, d\tau_1\, d\tau_2 \quad (7\text{-} \end{aligned}$$

where H is the same Hamiltonian written down above as (7-12) and N^2 $\frac{1}{2}(1 \pm S^2)^{-1}$. The terms resulting from the expansion of the integr are usually written as

$$E = 2E_{1s}(\mathrm{H}) + \frac{J}{1 \pm S^2} \pm \frac{K}{1 \pm S^2} \quad (7\text{-}$$

where $$J = \iint a(1)b(2)\left[-\frac{1}{R_{b1}} - \frac{1}{R_{a2}} + \frac{1}{r_{12}} + \frac{1}{R_{ab}}\right] a(1)b(2)\, d\tau_1\, d\tau_2 \quad (7\text{-}$$

and $$K = \iint a(1)b(2)\left[-\frac{1}{R_{b1}} - \frac{1}{R_{a2}} + \frac{1}{r_{12}} + \frac{1}{R_{ab}}\right] b(1)a(2)\, d\tau_1\, d\tau_2 \quad (7\text{-}$$

In analogy to the atomic case, J is called the *direct* integral and K the *excha* integral.

Expanding J and using symmetry, we obtain

$$J = -2\int \frac{a^2(1)\,d\tau_1}{R_{b1}} + \frac{1}{R_{ab}} + \iint \frac{a^2(1)b^2(2)}{r_{12}}\,d\tau_1\,d\tau_2 \tag{7-26}$$

This will be quite small, since it represents the Coulomb energy between two overlapping, classically distinguishable, spherically symmetric, neutral atoms. The first term is the attraction of the electron on each atom for the nucleus of the other, the second is the repulsion of the nuclei, and the third is the repulsion of the two electron clouds. If we expand K in a similar way, we find

$$K = -2S\int \frac{a(1)b(1)}{R_{b1}}\,d\tau_1 + \frac{S^2}{R_{ab}} + \iint \frac{a(1)b(2)b(1)a(2)}{r_{12}}\,d\tau_1\,d\tau_2 \tag{7-27}$$

These terms all have to do with the *exchange-charge density* $a(1)b(1)$. This is located in the overlap region between the nuclei, where a and b are simultaneously nonzero. The total exchange charge $\int a(1)b(1)\,d\tau_1 = S$, the overlap integral. To interpret (7-27) semiclassically, we note that we must reduce the nuclear charges from e to Se. Then the first term is the attraction of the exchange charge to the two nuclei, the second is the reduced nuclear repulsion due to the reduced nuclear charge, and the third is the electrostatic self-energy of the exchange-charge cloud. If a and b were orthogonal, only the last term would survive and it would be positive, as are all proper atomic exchange integrals. However, in hydrogen and all simple covalent bonds, S is sufficiently large and the distribution of exchange charge is such that the first term dominates and K is negative.

If we now refer back to our energy expression (7-23), we see that, because $K < 0$, the singlet state ${}^1\Sigma_g$ lies below the triplet ${}^3\Sigma_u$. This is, of course, correct and is the result we obtained earlier by considering molecular orbitals. Moreover, because $|K| > |J|$, the molecular energy lies below the energy of the separated atoms and the singlet state represents a bound molecule.

It is at this point that confusion often arises because of the complete difference in significance of this exchange integral K, and the exchange integrals of atomic theory. The latter include only the self-energy term of the exchange-charge cloud. Hence they are positive definite, and Hund's rule that the state of maximum S lies lowest follows. In the H-L case, however, the lack of orthogonality makes K negative. It is this term which lowers the energy to give the strong bonding in the ${}^1\Sigma_g$ state and raises the energy of the ${}^3\Sigma_u$ state. This apparent contradiction of the Hund rule is removed in the MO approach (which has only positive exchange integrals), since the ${}^3\Sigma_u$ state arises from an excited *configuration* in which one electron has been promoted from a σ_g to a σ_u orbital.

From this discussion, we see that there is no absolute signific exchange integrals or "exchange forces." All the forces are just Co interactions, and the exchange-charge densities depend on the mathem form of the wavefunction. If we express ψ in terms of orthogonal or for example, all exchange integrals are positive. With H-L orbitals, are negative. By suitable juggling, they could even be made to vanish. in all cases, if the method is carried through consistently, we get th final answers. In view of these facts, the frequently occurring stat that, if "the" exchange integral is positive, we have ferromagnetic cou (spins tend to be parallel), whereas if it is negative, we have antiferromag coupling (spins tend to be opposed), is seen to make sense only in so everyone refers to a rather standard setup with nonorthogonal orbit the H-L sort.

Despite the number of years that have passed since Heisenberg discussed the exchange interaction, efforts at clarifying these points still being vigorously pressed. A particularly penetrating review has been by Herring.[1] He shows that, although the H-L approximation redu correctly to the separated atoms at infinite distance, it does not become asym totically exact for singlet-triplet energy differences. In fact, when the int nuclear distance exceeds about 50 atomic units, the simple H-L theory le to the triplet lying *below* the singlet, which is simply not correct. He sugg a modified H-L method that *is* asymptotically exact at large distances. Fro it he finds that the coupling is always antiferromagnetic (singlet below tripl provided that the atomic wavefunctions have no angular nodes. He also able to justify the form of the Heisenberg–Dirac–Van Vleck vecto model coupling law (Sec. 6-4) in the asymptotic limit. For further di cussion of exchange, superexchange, and covalency, the reader is referred t the literature.[2]

7-7 Orthogonal Atomic Orbitals

The above discussion suggests that it might be interesting to consider making a H-L type of calculation using atomic orbitals so modified as to be orthogonal, unlike the normal 1*s* functions of hydrogen. This technique is similar to the introduction of Wannier functions[3] in solids. In the H_2 case, by symmetry we can simply take

$$A = C_1 a + C_2 b \qquad B = C_1 b + C_2 a \tag{7-28}$$

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[1] C. Herring, *Revs. Modern Phys.*, **34**, 631 (1962).

[2] See for example: P. W. Anderson, *Phys. Rev.*, **115**, 2 (1959), and a review article, Exchange in Insulators: Superexchange, Direct Exchange, and Double Exchange, in H. Suhl and G. Rado (eds.), "Magnetism," Academic Press Inc., New York, to be published; also R. K. Nesbet, *Phys. Rev.*, **122**, 1497 (1961); A. J. Freeman and R. E. Watson, *Phys. Rev.*, **124**, 1439 (1961).

[3] G. H. Wannier, *Phys. Rev.*, **52**, 191 (1937).

th C_1 and C_2 chosen to make A and B orthonormal. This requires

$$C_1 = \frac{1}{2(1+S)^{\frac{1}{2}}} + \frac{1}{2(1-S)^{\frac{1}{2}}} \qquad C_2 = \frac{1}{2(1+S)^{\frac{1}{2}}} - \frac{1}{2(1-S)^{\frac{1}{2}}}$$

nce S is reasonably small, C_1 is nearly 1 but C_2 is a small negative number $S/2$). The resulting functions are shown schematically in Fig. 7-5. he positive overlap in the middle is just canceled by the negative overlap ar the centers a, b.

Now, if one calculates the diagonal energy of the H-L $^1\Sigma_g{}^+$ ground state function built of these, namely,

$$\psi \sim A(1)B(2) + B(1)A(2) \tag{7-29}$$

one finds no binding at all! At no value of R_{ab} does the energy lie below that of the separated atoms. To get a decent energy, we must also form

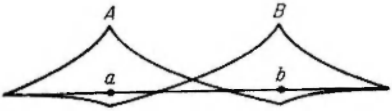

Fig. 7-5. *Schematic diagram of orthogonalized atomic orbitals for* H_2.

the other $^1\Sigma_g{}^+$ state, which will lie still higher in energy, and solve the secular equation between them. This configuration interaction, of course, will lead to exactly the same final functions and energies as we found using MO's with configuration interaction or using the ordinary H-L method with optimum admixture of ionic states. These methods differ only in their choice of initial approximate wavefunction. Our experience with these three methods now suggests that, for H_2 at least, the H-L method gives a slightly better initial approximation than the MO method, whereas the orthogonal atomic-orbital method gives a hopeless initial approximation. This latter fact points up the extreme importance of nonorthogonality for the success of the H-L method. Clearly caution must be exercised if any of the initial approximations is to be trusted.

7-8 Group Theory and Molecular Orbitals

In our discussion of H_2 we found it useful to note that there were no matrix elements of H between states belonging to different irreducible representations of the symmetry group of the molecule. This principle is even more useful in setting up MO's for the description of polyatomic molecules. If we set up LCAO's which are symmetry orbitals belonging to definite irreducible representations, these will factor the large secular equations which would otherwise occur.

In some cases, the symmetry orbitals can be set up by inspection. this fails, we can fall back on the *basis-function generating machine* (Sec. to produce suitable orbitals, given any function F (such as an atomic orb which one wants to use as part of the set of symmetry orbitals. Given complete representation matrices, symmetry orbitals belonging to partic rows of particular irreducible representations can be generated. If we given only the characters, we can only generate symmetry orbitals belong to a given representation. However, if we generate l suitably related in pendent functions of this sort, where l is the dimensionality, we can choo orthonormal combinations of these which can serve as basis functions the rows of a particular unitary representation. Thus it is always possi to get a large degree of help in choosing the symmetry orbitals, even w knowledge of only the characters.

Hückel theory. To see how these principles work out in practice, let consider the example of benzene, C_6H_6, first treated by use of molecu orbitals by Hückel.[1] This has the symmetry D_{6h}. So long as we con our attention to functions which are all even or all odd under σ_h, we n consider only the operations of D_6. (This is similar to the situation in o crystal-field work, where we could ignore the parity operator because were dealing with functions of a definite parity.) The character table f D_6 follows:

D_6	E	C_2	$2C_3$	$2C_6$	$3C_2'$	$3C_2''$
$\Gamma_1(A_1)$	1	1	1	1	1	1
$\Gamma_2(A_2)$	1	1	1	1	-1	-1
$\Gamma_3(B_1)$	1	-1	1	-1	1	-1
$\Gamma_4(B_2)$	1	-1	1	-1	-1	1
$\Gamma_5(E_2)$	2	2	-1	-1	0	0
$\Gamma_6(E_1)$	2	-2	-1	1	0	0
Γ_S	6	0	0	0	2	0

Figure 7-6 shows the location of typical C_2' and C_2'' axes and the labeling o the six carbon sites around the ring.

Now assume, for example, that we want to set up six orthonormal symmetry orbitals built from the six carbon $2s$ orbitals. Since these s functions transform into each other under D_6, they form a basis for a 6 dimensional representation Γ_S. By applying the same elementary considerations used earlier (Sec. 4-12) in discussing the valence-bond method, w can work out the character of Γ_S under all the group operations. This character has been written in at the bottom of the preceding character table

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[1] E. Hückel, *Z. Physik*, **70**, 204 (1931).

From this character we then deduce that

$$\Gamma_S = \Gamma_1 + \Gamma_3 + \Gamma_5 + \Gamma_6 \tag{7-30}$$

Thus we can form two nondegenerate symmetry orbitals and two pairs of doubly degenerate symmetry orbitals from our six atomic orbitals.

We next work out these symmetry orbitals explicitly. Since Γ_1 is the totally symmetric representation, the corresponding orbital can be written down by inspection as being

$$\psi(\Gamma_1) \sim [a + b + c + d + e + f]$$

Normalizing, with allowance for a nearest-neighbor overlap integral S, we have

$$\psi_1 = \psi(\Gamma_1) = [6(1 + 2S)]^{-1/2}(a + b + c + d + e + f) \tag{7-31}$$

where $a, b, \ldots$ are the atomic functions located on the corresponding carbon centers.

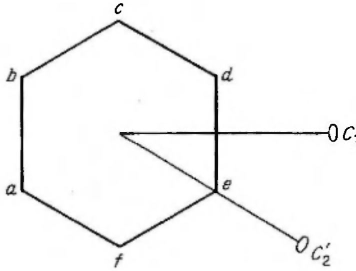

Fig. 7-6. *Geometry of benzene structure.*

The function belonging to Γ_3 is obtained by using the basis-function generating technique applied to, for example, a. Thus using (3-38),

$$\begin{aligned}\psi(\Gamma_3) &\sim \sum_R \chi^{(3)}(R)P_R a\\ &= 1 \cdot Ea - 1 \cdot C_2 a + 1\sum C_3 a - 1\sum C_6 a + 1\sum C_2' a - 1\sum C_2'' a\\ &= a - d + (c + e) - (b + f) + (a + e + c) - (f + b + d)\\ &= 2(a - b + c - d + e - f)\end{aligned}$$

Normalizing, we obtain

$$\psi_2 = \psi(\Gamma_3) = [6(1 - 2S)]^{-1/2}(a - b + c - d + e - f) \tag{7-32}$$

For Γ_5, we have to deal with a two-dimensional representation. Therefore we must generate two independent functions. If we do this by operating on a and on b, we find

$$\psi_3' \sim (2a + 2d - c - e - b - f)$$
$$\psi_4' \sim (2b + 2e - a - c - d - f)$$

These functions are not orthogonal as they stand. However, if one the sum and difference $\psi_3' \pm \psi_4'$, one obtains two orthogonal functions easy to show that the sum and difference of any two similarly norm real functions are orthogonal.) After normalization, these ortho functions are

$$\psi_3 = [4(1 - S)]^{-\frac{1}{2}}(a - b + d - e) \qquad (7$$

$$\psi_4 = [12(1 - S)]^{-\frac{1}{2}}(a + b - 2c + d + e - 2f) \qquad (7$$

These functions then can be taken as the basis functions for the two-d sional unitary representation Γ_5. In a similar way, we find the follo basis for Γ_6:

$$\psi_5 = [4(1 + S)]^{-\frac{1}{2}}(a + b - d - e) \qquad (7-$$

$$\psi_6 = [12(1 + S)]^{-\frac{1}{2}}(a - b - 2c - d + e + 2f) \qquad (7-$$

In this simple way we have found a unitary transformation between six atomic orbitals and six molecular-symmetry orbitals, all belongin different rows of irreducible representations. Therefore there are no m elements of the Hamiltonian between them, and the 6 × 6 secular equat based on the six AO's has been factored completely by symmetry alo If the matrix elements between the AO's are known, the energies of the M can be written down directly. For example, if we assume that the diago energy of the AO's is

$$(a\,|H|\,a) = (b\,|H|\,b) = \cdots = Q \qquad (7-$$

and that only nearest-neighbor AO's have matrix elements β between the so that

$$(a\,|H|\,b) = (b\,|H|\,c) = \cdots = (f\,|H|\,a) = \beta \qquad (7-3$$

then we have

$$\begin{aligned} W(\Gamma_1) &= (\psi_1\,|H|\,\psi_1) \\ &= [6(1 + 2S)]^{-1}(a + b + c + d + e + f\,|H|\,a + b + c + d + e + f) \\ &= \frac{Q + 2\beta}{1 + 2S} \qquad (7\text{-}37a) \end{aligned}$$

Similarly,

$$W(\Gamma_3) = \frac{Q - 2\beta}{1 - 2S} \qquad (7\text{-}37b)$$

$$W(\Gamma_5) = \frac{Q - \beta}{1 - S} \qquad (7\text{-}37c)$$

$$W(\Gamma_6) = \frac{Q + \beta}{1 + S} \qquad (7\text{-}37d)$$

Since the nodeless totally symmetric MO is expected to lie lowest, β is presumably negative. S is expected to be positive, since the overlapping outer parts of all the atoms have the same sign. The complete level scheme then as shown in Fig. 7-7. For simplicity, the figure is drawn with ne-t of S compared with β/Q. Three levels are depressed below the AO rgy, and three are raised above it. If, for example, we have a single $2s$ tron contributed by each atom, the electrons will doubly occupy (two in orientations) the lower three levels. This total decrease in energy would the binding energy of the molecule arising from the $2s$ electrons. If ch atom contributed two $2s$ electrons, all levels would be filled and no

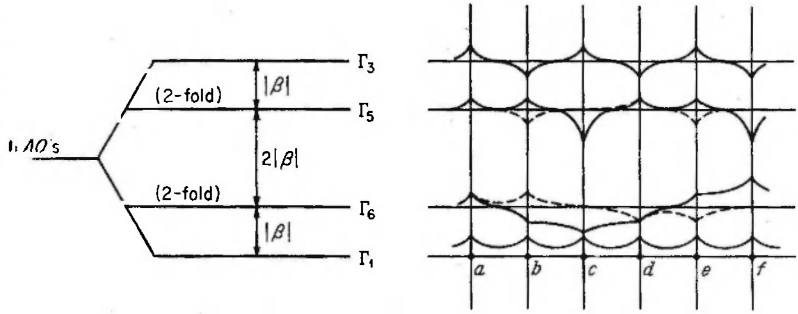

Fig. 7-7. *Molecular-orbital energy-level scheme for benzene, with overlap integrals neglected. The form of the MO is also shown schematically in each case, a* 1*s atomic orbital being used for simplicity. In case of degeneracy, the two functions are distinguished by solid and dashed curves.*

first-order contribution to binding would occur according to these results. In fact, some repulsion would occur, as expected for closed-shell atoms. Including higher terms in (7-37), this calculation shows an upward shift of the center of gravity of the levels by an amount $2\,|\beta|\,S + 2QS^2 + \cdots$, which increases with increasing overlap.

One might wonder how our Γ_6 wavefunctions display the symmetry of the molecule, since in neither ψ_5 nor ψ_6 is there the same amount of charge on all six equivalent centers. However, since these two functions are degenerate, they will be equally occupied and $|\psi_5|^2 + |\psi_6|^2$ does have equal charge on all centers, as required by the generalized Unsöld theorem (see Sec. 4-9).

Additional insight into these wavefunctions can be obtained by noting that the cyclic group of order 6 is a subgroup of the full symmetry of this system. Thus the eigenfunctions of the Hamiltonian can be chosen from those of the cyclic group, the generating element of the group being a rotation by $\pi/3$ about the center of the benzene ring. Thus by the Bloch theorem (3-26), we must have

$$\psi_n\left(\varphi + \frac{\pi}{3}\right) = e^{i\pi n/3}\psi_n(\varphi)$$

where φ is an angle of rotation in the plane of the molecule and n tak values 0, 1, 2, 3, 4, 5. We can construct such a function (not normal by taking

$$\psi_n(\mathbf{r}) = \sum_{q=1}^{6} e^{in\pi q/3} a_q(\mathbf{r})$$

(7

where a_q is an AO located on the qth site around the ring. These func ψ_n represent progressive waves, traveling around the ring. Note that functions for $n = 0$ and 3 correspond to the functions found in (7-31) (7-32) for Γ_1 and Γ_3, respectively. The functions for $n = 2$ and 4 are generate, being complex conjugates of each other. Taking the real imaginary parts separately, corresponding to standing waves, one finds functions found in (7-33) for Γ_5. Similarly, ψ_1 and ψ_5 lead to the Γ_6 fu tions. Thus the eigenfunctions found earlier are closely related to Blo functions for this cyclic "crystal" containing only six atoms.

So far we have considered LCAO symmetry orbitals derived only fro the carbon $2s$ functions. Exactly the same calculations would carry throu for the carbon $1s$ and hydrogen $1s$ functions. We have to be a bit mo careful with the carbon $2p$ functions, since they are not invaria under rotations. The six p_R functions, directed radially, will transfor exactly like the S functions under D_{6h}, and hence they will form the sa kind of symmetry orbitals. The six p_π functions normal to the plane the molecule belong to representations of the full D_{6h} group which are o under σ_h. Hence, this type of π electron will not mix at all with those wh are even under σ_h, but they will still be split into four levels: Γ_2^-, Γ_4^-, Γ Γ_6^-. Finally, the "tangential" p_π orbitals in the plane will form a six-dime sional representation which can be reduced to Γ_2^+, Γ_4^+, Γ_5^+, Γ_6^+,

Now we are ready to put the pieces together to get the best wavefunctio for the C_6H_6 molecule as a whole. We have found a set of 36 symmet orbitals which can be formed from the 36 low-lying AO's of the types H(1 and C($1s$, $2s$, $2p$). These are distributed among the irreducible represent tions as follows:

Γ_1^+ and Γ_3^+: H($1s$)C($1s$)C($2s$)C($2p_R$)

Γ_2^+ and Γ_4^+: C($2p_T$)

Γ_5^+ and Γ_6^+: H($1s$)C($1s$)C($2s$)C($2p_R$)C($2p_T$)

Γ_2^-, Γ_4^-, Γ_5^-, and Γ_6^-: C($2p_\pi$)

Allowing for spin orientation, we thus have 72 possible states into which to put the 42 electrons of the benzene molecule. The problem is to find the 42 lowest-lying MO's into which to put the electrons to form the ground state. These "best" MO's will not in general be identical with the symmetry orbitals which we have found, but rather optimum (via the variational nciple) linear combinations of those of the same symmetry. We find the optimum combinations by solving the secular equation between the rious symmetry orbitals of the same symmetry. (Matrix elements are owed between these because they belong to the same row of the same irreucible representation.) These secular equations are relatively tiny, however, and therefore easy to solve. In our example, the largest secular uations would be the 5 × 5's from Γ_5^+ and Γ_6^+, whereas the unfactored oblem working with AO's would involve solving a 36 × 36! Even the × 5 can be reduced for practical purposes to a 4 × 4 because the diagonal energy of the C(1s) symmetry orbital will lie so far below that of the others that the slight mixing with the others can be handled by perturbation theory, if at all. In fact it is often assumed that such "inner-shell" symmetry orbitals are exact enough to be considered occupied and unperturbed and simply left out of the problem from the start.

After these small secular equations have been solved, we shall have determined the 36 MO's which are the best approximations to the true eigenfunctions which can be formed from the 36 atomic orbitals which we started with. The MO's are all orthogonal and can be treated much like the one-electron functions of atomic physics. To get the ground configuration, these are filled by starting from the lowest-lying level and working up till all the electrons are accounted for. Excitation and ionization energies are determined from the differences of one-electron MO energies. There is, however, little of the zero-order degeneracy within a configuration, which gives the L-S terms in atomic structure, because the low symmetry of the molecule severely restricts the maximum dimensionality of the irreducible representations.

Naturally, the outline given here can indicate only the barest skeleton of the modern methods for calculating molecular energy levels by the method of molecular orbitals. However, useful results in the interpretation of experimental data can be obtained even with this simple framework. For more details about realistic calculation methods, including those using the full Hartree-Fock formalism, the reader is referred to the literature.[1]

7-9 Selection Rules for Electronic Transitions

Linear molecules $C_{\infty v}$. For linear molecules, the z component of the dipole moment belongs to the Σ^+ (or A_1) representation, while the x and y components belong to the Π (or E_1) representation. Since the direct product of any representation Γ with A_1 simply reproduces Γ, the selection rules for transitions induced by the z component of the dipole mo

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[1] See, for example, C. C. J. Roothan, *Revs. Modern Phys.*, **23**, 69 (1951); A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, 1961; R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry," Interscience Publishers, Inc., New York, 1959.

$$\Sigma^+ \to \Sigma^+ \qquad \Sigma^- \to \Sigma^- \qquad \Pi \to \Pi \qquad \Delta \to \Delta \qquad \text{etc.}$$

The x, y polarization case is worked out by noting that $\chi^{(\Pi)}(C_\varphi) = 2$ and in general $\chi^{(\Lambda)}(C_\varphi) \sim \cos \Lambda\varphi$. Thus, the direct-product char proportional to $\cos \varphi \cos \Lambda\varphi$, hence to $[\cos (\Lambda + 1)\varphi + \cos (\Lambda - 1)\varphi$ the selection rule is $\Delta\Lambda = \pm 1$. Combining this result with that for component, we have the following selection rules for unpolarized ra or randomly oriented molecules:

$$\Sigma^+ \leftrightarrow \Sigma^+, \Pi$$
$$\Sigma^- \leftrightarrow \Sigma^-, \Pi$$
$$\Pi \leftrightarrow \Sigma^+, \Sigma^-, \Pi, \Delta$$
$$\Delta \leftrightarrow \Pi, \Delta, \Phi$$

Homonuclear diatomic molecules $D_{\infty h}$. In this case, z belongs to Σ_u (x, y) to Π_u. Since $D_{\infty h}$ can be considered to be the direct product o with the inversion, nothing new is added to the selection rules found except that there must be a parity change in each case because the el dipole operator has odd parity. For example, we have $\Sigma_g^+ \leftrightarrow \Sigma_u^+, \Pi_u$ $\Sigma_u^+ \leftrightarrow \Sigma_g^+, \Pi_g$.

Polyatomic molecules. One must find the representations to which and z belong for the symmetry group of the molecule under consider and must use these in direct products to find the selection rules. For example of benzene, treated in the previous section, z belongs to Γ_2 (x, y) belong to Γ_6. Thus, by inspecting the character table, we see transitions induced by the z component of the dipole moment are allo for $\Gamma_1 \leftrightarrow \Gamma_2$, $\Gamma_3 \leftrightarrow \Gamma_4$, $\Gamma_5 \leftrightarrow \Gamma_5$, and $\Gamma_6 \leftrightarrow \Gamma_6$. Similarly, transitions ind by x and y components connect the following: Γ_1, $\Gamma_2 \leftrightarrow \Gamma_6$; Γ_3, $\Gamma_4 \leftrightarrow$

7-10 Vibration of Diatomic Molecules

Now that we have examined methods for handling the problems of electronic motion in a molecule with fixed nuclear force centers, we n proceed in the Born-Oppenheimer approximation to study the nuclear mo in the effective potential provided by the electronic energy. The Ha tonian for this stage in the problem is

$$H = \sum_\alpha \frac{\mathbf{P}_\alpha^2}{2M_\alpha} + V(\mathbf{R}_\alpha) \qquad (7\text{-}$$

The effective potential here, $V(\mathbf{R}_\alpha)$, is to be identified with the total electr energy as a function of internuclear distance $E_e(\mathbf{R}_\alpha)$, which includes, as (7-2), the direct internuclear-repulsion energy $V_{nn}(\mathbf{R}_\alpha)$.

To fix ideas, we again specialize to the simplest type of molecules, mely, diatomic (but not necessarily homonuclear) molecules. As is well wn, the kinetic-energy term may be separated into three parts: (1) center-mass motion (three degrees of freedom), (2) rotation (two degrees), and) vibration (one degree). The terms here are listed in ascending order in rgy. We now concentrate on the vibrational part. This is equivalent the problem of a one-dimensional oscillator with *reduced mass* $\mu =$ $_1M_2/(M_1 + M_2)$ and a restoring force derived from the effective potential $R) \quad E_e(R)$ obtained from the solution for the electronic energy as a nction of R. This effective potential has the general form shown in g. 7-2.

The simplest approximation is to treat $V(R)$ as a parabola about R_e. his is quite good for small oscillations but becomes quite hopeless as one proaches dissociation. Since the solution of the harmonic oscillator is miliar from elementary quantum mechanics,[1] it will not be repeated here. uffice it to say that the resulting energy levels are

$$E_v = (v + \tfrac{1}{2})\hbar\omega_e \tag{7-40}$$

here ω_e is the classical vibration frequency of the oscillator and $v = 0, 1,$ 2, . . . is the vibrational quantum number. Both position and momentum operators have $\Delta v = \pm 1$ matrix-element selection rules.

The Morse approximation. The most famous and generally useful higher approximation for the molecular-vibration problem is that of Morse.[2] He sought an analytic approximation to the effective potential $V(R)$ which would have all the correct qualitative features built in. That is, he wanted a function $V(R)$ that approached a constant as $R \rightarrow \infty$, became very large (preferably infinite) as $R \rightarrow 0$, had a minimum at some equilibrium point R_e, and led to an exactly soluble Schrödinger equation with eigenvalues departing from the equally spaced harmonic-oscillator ones in the experimentally observed manner. He satisfied these requirements by the choice

$$V(R) = D_e[1 - e^{-a(R-R_e)}]^2 \tag{7-41}$$

which has the zero of energy at the minimum of the potential at R_e. As $R \rightarrow \infty$, $V(R) \rightarrow D_e$, the dissociation energy. The parameter a controls the curvature at the minimum by setting the scale of radial distance. As $R \rightarrow 0$, $V(R) \rightarrow D_e[1 - e^{aR_e}]^2 \approx D_e e^{2aR_e} \gg D_e$. In fact, $V(0)$ should be infinite because of the $Z_1Z_2\, e^2/R$ Coulomb repulsion. However, as long as $V(0) \gg D_e$, no serious error results from finiteness of $V(0)$.

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[1] See, for example, L. I. Schiff, "Quantum Mechanics," 2d ed., p. 60, McGraw-Hill Book Company, Inc., New York, 1955.

[2] P. M. Morse, *Phys. Rev.*, **34,** 57 (1929).

Upon putting (7-41) into (7-39), setting up the Schrodinger equ
and separating variables, the radial equation to be solved is

$$-\frac{\hbar^2}{2\mu}\frac{d^2S}{dR^2} + \left\{\frac{J(J+1)\hbar^2}{2\mu R^2} + D_e[1 - e^{-a(R-R_e)}]^2\right\} S = ES \qquad (7$$

where $\psi(\mathbf{R}) = R^{-1}S(R)Y_J^M(\theta, \varphi)$ is the complete wavefunction, on
assumption that the rotational quantum number is J. The term

$$J(J+1)\hbar^2/2\mu R^2$$

is the *centrifugal potential* arising from rotation. Since it is of a sm
order of magnitude than the term in D_e, we shall neglect it for the t
being, treating only the purely vibrational energy of a nonrotating vib
In this case, an exact solution to (7-42) may be obtained by making a cha
of variable by defining

$$x = e^{-a(R-R_e)} \qquad (7$$

leading to

$$\frac{d^2S}{dx^2} + \frac{1}{x}\frac{dS}{dx} + \frac{2\mu}{a^2\hbar^2}\left(\frac{E - D_e}{x^2} + \frac{2D_e}{x} - D_e\right)S = 0 \qquad (7-$$

This equation can be solved in terms of the associated Laguerre polynom
(which also appear in solving the radial equation for the hydrogen ato
Since the resulting wavefunction is not of much use, it will not be quo
here. It is important to note only that the usual requirement of trunca
a series to a polynomial to satisfy boundary conditions leads to a quant
condition for the energy eigenvalues. The resulting energy levels are

$$E_{\text{vib}} = \hbar\omega_e(v + \tfrac{1}{2}) - x_e\hbar\omega_e(v + \tfrac{1}{2})^2 \qquad (7-$$

with

$$\omega_e = a\left(\frac{2D_e}{\mu}\right)^{\frac{1}{2}} \qquad (7-4$$

and

$$x_e = \left(\frac{\hbar\omega_e}{4D_e}\right) \qquad (7-4$$

The first term of (7-45) is obviously the ordinary harmonic-oscillator appro
mation, while the second gives a correction due to the "softening" of t
restoring potential for large amplitudes. In fact, it was known empiric
that experimental data fit the form (7-45) quite accurately, and Morse view
this agreement as demonstrating that (7-41) did in fact give a quite go
approximation to the true potential curve. This point has been verified
more detail by constructing numerically a potential function which d
reproduce the experimental levels exactly and comparing it with the Mor
curve.[1]

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[1] See, for example, O. Klein, *Z. Physik*, **76**, 226 (1932); R. Rydberg, *Z. Physik*, **73**, 3 (1932), **80**, 514 (1933); A. L. G. Rees, *Proc. Phys. Soc.* (*London*), **59**, 998 (1947); H. Hulburt and J. O. Hirshfelder, *J. Chem. Phys.*, **9**, 61 (1941).

It is interesting to note that the eigenvalues (7-45) reach a maximum of just D_e, the dissociation energy, when $(v + \frac{1}{2}) = \frac{1}{2}x_e^{-1} = 2D_e/\hbar\omega_e$. Thus, there are a finite number of discrete vibrational levels for this problem, and because of the crowding together of the upper levels, this number is just twice what it would be if the level spacing remained $\hbar\omega_e$ all the way up to the dissociation energy D_e.

Other approximations. Although the Morse approximation is probably that most often used, many others have been suggested by various authors. The first serious attempt at treating the anharmonic molecular oscillator was that of Kratzer,[1] using old quantum theory. This type of power-series approach, where one takes

$$V(R) = V(R_e) + \tfrac{1}{2}V''(R_e)(R - R_e)^2 + \tfrac{1}{6}V'''(R_e)(R - R_e)^3 + \cdots \qquad (7\text{-}46)$$

was carried into wave mechanics by Dunham,[2] later simplified and extended by Sandeman.[3] This method enables one to obtain as good an approximation near R_e as desired, by simply taking more terms, and the solution is quite straightforward by using perturbation methods. However, the method works badly far from R_e, since the expansion (7-46) inevitably diverges as $R \to \infty$, rather than approaching a constant D_e.

To show how the method works, let us consider a case where only one anharmonic term is carried and take our zero of energy to be at $V(R_e)$. Then we can write

$$V(\xi) = a_2\xi^2 + a_3\xi^3 \qquad (7\text{-}47)$$

where

$$\xi = \frac{(R - R_e)}{R_e}$$

is a normalized dimensionless vibrational coordinate and $a_2 = \frac{1}{2}\mu\omega_e{}^2R_e{}^2$. The matrix elements of ξ in the harmonic-oscillator approximation (neglect of a_3) are simply[4]

$$(v'\,|\xi|\,v) = \lambda[(v + 1)^{\frac{1}{2}}\delta_{v',v+1} + v^{\frac{1}{2}}\delta_{v',v-1}] \qquad (7\text{-}48)$$

where

$$\lambda = \left(\frac{\hbar}{2\mu R_e{}^2\omega_e}\right)^{\frac{1}{2}}$$

Knowing the matrix of ξ, one can calculate the matrices of ξ^2, ξ^3, . . . by simple matrix multiplication. Thus

$$(v'\,|\xi^2|\,v) = \lambda^2\{[(v + 1)(v + 2)]^{\frac{1}{2}}\delta_{v',v+2} + (2v + 1)\delta_{v',v} + [v(v - 1)]^{\frac{1}{2}}\delta_{v',v-2}\} \qquad (7\text{-}49)$$

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[1] A. Kratzer, *Z. Physik*, **3**, 289 (1920).

[2] J. L. Dunham, *Phys. Rev.*, **41**, 713, 721 (1932).

[3] I. Sandeman, *Proc. Roy. Soc. Edinburgh*, **60**, 210 (1940).

[4] See, for example, Schiff, *op. cit.*, p. 65.

and

$$(v' |\xi^3| v) = \lambda^3\{[(v+1)(v+2)(v+3)]^{\frac{1}{2}}\delta_{v',v+3}$$
$$+ 3(v+1)^{\frac{3}{2}}\delta_{v',v+1} + 3v^{\frac{3}{2}}\delta_{v',v-1} + [v(v-1)(v-2)]^{\frac{1}{2}}\delta_{v',v-3}\}.$$

Combining these with the matrix for the kinetic energy ($P^2/2\mu$), we

$$(v' |H| v) = (v + \tfrac{1}{2})\hbar\omega_e\delta_{v'v} + a_3(v' |\xi^3| v)$$

Calculating the anharmonic correction to second-order perturbation leads to

$$E(v) = (v + \tfrac{1}{2})\hbar\omega_e - \frac{30a_3{}^2\lambda^6}{\hbar\omega_e}(v + \tfrac{1}{2})^2 + \text{const}$$

Thus, to this order of perturbation theory, we find the same form of as found with the Morse potential, namely, (7-45). The present focuses on the initial anharmonicity near $R = R_e$, whereas the Morse gives an overall approximation for the potential all the way out to dissoc

Numerous other potentials have been proposed, with three, four, or adjustable parameters. Each of these has its own advantages and be considered. In particular, it should be pointed out that some of are definitely superior in agreement with experiment to the Morse pot which has perhaps been overworked because of its simplicity and invention. For a critical survey of almost two dozen such functions reader is referred to a review article by Varshni.[1]

7-11 Normal Modes in Polyatomic Molecules

Let us consider the motion of N nuclei in a general molecule as governe the energy function $V(\mathbf{R}_\alpha)$ determined by solution of the electronic probl We specify the position of all the nuclei by giving $3N$ coordinates ξ_k, measured from the equilibrium position of the relevant nucleus. Th fore the energy V will have its minimum value if all the coordinates are and will increase no faster than quadratically as any coordinate departs zero. That is, there can be no linear term, since this would contradict assumed equilibrium. However, there will certainly be anharmonic te ($\sim\xi_k{}^3$, etc.) which need to be considered for large ξ_k. These anharmo terms introduce coupling between the normal modes, which could be trea as correction terms. These coupling terms, for example, allow therm equilibrium to be reached after a single mode is excited, a process which co not occur if the modes were truly independent. For the time being, howev we shall neglect these terms and shall consider the decomposition of possible motions of the nuclei into independent normal modes of vibratio The group theory is very helpful in finding the particular combinatio

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[1] Y. P. Varshni, *Revs. Modern Phys.*, **29**, 664 (1957).

$= \sum_k a_{kK}\xi_k$ which describe the normal modes of a molecule of given symmetry.

A geometrical viewpoint may be helpful in an initial consideration of the modes. We view the set of $3N$ ξ_k's as the coordinates of a point in a dimensional phase space. In the equilibrium position the phase point is at the origin. Now, for any small distortion or displacement of the molecule, there is a corresponding small displacement of the representative point in some direction from the origin to the point $(\xi_1 \cdots \xi_{3N})$. Knowing $V(\xi_k)$, we can compute the increase in potential energy for any small motion in this $3N$-dimensional space. Obviously, if we impart a uniform translation in physical space to the molecule as a whole, there is no increase in potential energy, and hence no restoring force. Similarly, a uniform rotation produces no potential energy or restoring force. Thus there are six independent $3N$-dimensional vector displacements which can be made with no restoring force. (There are only five for a linear molecule, because only two angles are required to specify the rotational orientation.) For example, a displacement of the molecule by (Δz) in the z direction would be given by a phase-space vector displacement $\boldsymbol{\xi} = (\Delta z)[\mathbf{u}_3 + \mathbf{u}_6 + \cdots + \mathbf{u}_{3N}]$ where the $\mathbf{u}_k$ are unit vectors representing displacements of individual particles along one of the cartesian axes.

We now imagine that the system has been given an arbitrary displacement from the origin in any direction orthogonal to the six (or five, for linear molecules) directions in which there is no restoring force. The motion which ensues after the system is released is in general a complicated one, with various coordinates vibrating irregularly with a variety of superposed frequencies. However, there exist $(3N - 6)$ [or $(3N - 5)$] orthogonal phase-space vectors $\mathbf{Q}_K$ defining directions such that the ensuing motion after a displacement along any one of them is a simple harmonic oscillation of frequency ω_K. These vectors define the normal modes of the system. Since they span the space of all displacements (when combined with the six translational and rotational vectors), an arbitrary motion can be represented as a sum over normal modes.

These normal coordinates Q_K are defined mathematically as the linear combinations of the ξ_k which bring the kinetic and potential energies, T and V, simultaneously to the diagonal forms

$$T = \tfrac{1}{2}\sum_{K=1}^{3N}(\dot{Q}_K)^2 \qquad V = \tfrac{1}{2}\sum_{K=1}^{3N}\omega_K{}^2 Q_K{}^2 \tag{7-53}$$

where $\dot{Q}_K = dQ_K/dt$. (The lack of restoring forces for translation and rotation makes six of the ω_K equal zero.) Introducing the canonical momentum by

$$P_K \equiv \frac{\partial T}{\partial \dot{Q}_K} \tag{7-54}$$

which in this case is simply Q_K, the classical Hamiltonian of the pro consists of a sum of terms, each dealing with only one mode, namely,

$$\begin{aligned} H &= T + V \\ &= \sum_{K=1}^{3N} H_K = \sum_{K=1}^{3N} \tfrac{1}{2}(P_K^2 + \omega_K^2 Q_K^2) \qquad \text{(7} \end{aligned}$$

Then, using the Hamilton canonical equation

$$P_K = -\frac{\partial H}{\partial Q_K} \qquad \text{(7}$$

we are led to

$$\ddot{Q}_K + \omega_K^2 Q_K = 0 \qquad \text{(7}$$

which has the solution

$$Q_K = Q_K^0 \cos(\omega_K t + \varphi) \qquad \text{(7}$$

where φ is an arbitrary phase angle.

The corresponding quantum-mechanical problem is also trivial, sin simple product solution, with one factor for each term in H, is succes That is, if we consider

$$H\Psi = \left(\sum_K H_K\right)\prod_K \psi_K(Q_K) = E\Psi$$

and divide through by Ψ, we have

$$\sum_K \frac{H_K \psi_K}{\psi_K} = E$$

Since each term in the sum depends only on one Q_K, all Q_K being indepen variables, the sum can equal the constant E only if each term is itself a c stant, E_K, say. Thus we have $3N$ equations of the form

$$H_K\psi_K = \tfrac{1}{2}(P_K^2 + \omega_K^2 Q_K^2)\psi_K = E_K\psi_K \qquad \text{(7-}$$

to determine $\Psi = \prod_K \psi_K(Q_K)$ and the equation

$$E = \sum_K E_K$$

to determine the system energy. Using the well-known solution for harmonic oscillator in quantum theory, we then have

$$E = \sum_K (v_K + \tfrac{1}{2})\hbar\omega_K \qquad \text{(7-}$$

and

$$\Psi = \prod_K N_{v_K} H_{v_K}(\alpha_K Q_K) e^{-(\alpha_K^2 Q_K^2/2)} \qquad \text{(7-}$$

where the H_{v_K} are Hermite polynomials, $\alpha_K{}^2 = \omega_K/\hbar$, and the N_{v_K} are normalizing constants. Thus, whether we use classical or quantum mechanics to treat the vibrational problem, once the normal coordinates Q_K which throw H into the form (7-55) are found, the problem is largely solved.

Let us now look more closely at the process of determining the transformation relating the Q_K to the ξ_k. First of all, it is convenient to transform from the ξ_k to "mass-weighted" coordinates

$$q_k = \sqrt{m_k}\,\xi_k \tag{7-62}$$

where m_k is the mass of the atom having displacement ξ_k. In terms of the q_k, the Hamiltonian is transformed from

$$H = \sum_k \tfrac{1}{2} m_k \dot{\xi}_k{}^2 + \sum_{k,l} \frac{1}{2} \frac{\partial^2 V}{\partial \xi_k \, \partial \xi_l} \xi_k \xi_l$$

to

$$H = \sum_k \tfrac{1}{2} \dot{q}_k{}^2 + \sum_{k,l} \frac{1}{2} \frac{\partial^2 V}{\partial q_k \, \partial q_l} q_k q_l$$

or

$$H = \sum_k \tfrac{1}{2} p_k{}^2 + \sum_{k,l} \tfrac{1}{2} f_{kl} q_k q_l \tag{7-63}$$

Since the kinetic-energy term is now expressed as a simple sum of squares, any orthogonal transformation of coordinates will preserve this form. To verify this, let us consider new coordinates defined by an orthogonal transformation a_{kK} so that

$$q_k = \sum_k a_{kK} Q_K \tag{7-64a}$$

$$Q_K = \sum_k (a^{-1})_{Kk} q_k = \sum_k a_{kK} q_k \tag{7-64b}$$

Then $\displaystyle \sum_k q_k{}^2 = \sum_{k,K,L} a_{kK} Q_K a_{kL} Q_L = \sum_{K,L} \left(\sum_k a_{kK} a_{kL} \right) Q_K Q_L$

$$= \sum_{K,L} \left(\sum_k (a^{-1})_{Kk} a_{kL} \right) Q_K Q_L = \sum_{K,L} \delta_{KL} Q_K Q_L = \sum_K Q_K{}^2$$

Since the transformation a_{kK} is independent of time, the same transformation holds for the $\dot{q}_k$ or for the p_k and this proof shows that $\sum_k p_k{}^2 = \sum_K P_K{}^2$, as was desired.

Since the kinetic energy retains its desired simple form under an arbitrary orthogonal transformation, one is free to choose a_{kK} so as to reduce the potential energy to a sum of squared terms with no cross terms. Applying the transformation to the potential-energy term in (7-63), we obtain

$$V = \tfrac{1}{2} \sum_{k,l,K,L} f_{kl} a_{kK} a_{lL} Q_K Q_L$$

$$= \tfrac{1}{2} \sum_{KL} [\mathbf{a}^{-1}\mathbf{f}\mathbf{a}]_{KL} Q_K Q_L$$

We want this to equal a sum of terms of the form $\frac{1}{2}\omega_K{}^2 Q_K{}^2$. This wi true if

$$[\mathbf{a}^{-1}\mathbf{f}\mathbf{a}]_{KL} = \omega_K{}^2 \delta_{KL}$$

After some rearrangement, this can be written

$$\sum_l [f_{kl} - \omega_K{}^2 \delta_{kl}] a_{lK} = 0 \qquad k = 1, 2, \ldots, 3N \qquad (7$$

For a nontrivial solution to these equations, ω_K must satisfy the sec equation

$$|f_{kl} - \omega_K{}^2 \delta_{kl}| = 0 \qquad (7$$

and, for each such ω_K, there is determined a set of coefficients a_{lK} defin a normal mode. When normalized and combined, these sets of a_{lK} de mine the entire transformation matrix **a**. One can show that six (or five linear molecules) of these ω_K are zero. These correspond to the mo which represent simple translation or rotation of the molecule. Sin is an orthogonal matrix, all other modes (i.e., those with $\omega_K \neq 0$) must orthogonal to those of zero frequency.

Although these mass-weighted cartesian coordinates simplify the gen theory nicely, they are not usually the most practical for calculation. O can work directly with nonweighted cartesian coordinates with only a sli change in the secular equation. However, the coordinate transformat is no longer orthogonal. More generally, one can use noncartesian co dinates η_k in which there are cross terms in the kinetic energy as well as in potential energy. Still, a generalized secular equation will determine eigenfrequencies.

A particularly useful approach is the use of *internal coordinates.* this method, one eliminates the six redundant coordinates at the very ginning, by using only coordinates internal to the molecule (such as bo lengths and angles). This reduces the size of the secular equation fr $3N \times 3N$ to $(3N - 6) \times (3N - 6)$, which will usually greatly simplify solution. Treating this method in detail would take us too far afield. refer the reader to the excellent book of Wilson, Decius, and Cross[1] fo thorough treatment, including numerous examples.

7-12 Group Theory and Normal Modes

Let us now consider the implications of molecular symmetry for the nat and degeneracy of the normal modes discussed in a general way in previous section. For geometric consideration of these modes, it is oft convenient to think in terms of unit vectors Q_K associated with the norm coordinates Q_K. As long as the matrix relation between q_k and Q_K is orthogonal, the same matrix **a** relates $\bar{q}_k$ to Q_K. Thus the two viewpoints can be exchanged quite freely. The unit vector O_K when decomposed in terms of the q_k indicates the displacements of each atom in the normal mode of vibration. If these displacements are depicted by small arrows on a diagram of the molecular framework, then the effect of symmetry operations can be readily seen by inspection.

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[1] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," chap. McGraw-Hill Book Company, Inc., New York, 1955.

Since a molecule is not fundamentally changed by applying a symmetry operator P_R, the mode $P_R Q_K$ must have the same frequency as Q_K itself. Thus, if Q_K is nondegenerate, then $P_R Q_K = \pm Q_K$, for all P_R, and Q_K forms the basis for a one-dimensional representation of the symmetry group of the molecule. However, if Q_K is degenerate, we can say only that

$$P_R \hat{Q}_K = \sum_{K'} Q_{K'} D(R)_{K'K} \tag{7-67}$$

where K' runs over all the modes degenerate with K. This is true because any linear combination of degenerate Q_K will oscillate at the same frequency ω_K. Thus, degenerate vibrational modes transform according to irreducible representations of dimensionality greater than 1, whereas nondegenerate modes correspond to one-dimensional representations.

This fact allows us to find the number of distinct vibrational frequencies ω_K and their degeneracy by decomposing the $3N$-dimensional representation of the symmetry group of the molecule which is based on three orthogonal unit vectors on each nucleus. After dropping the representations which account for translation and rotation, the remaining ones must all correspond to vibrational frequencies. Since there can be no coupling between modes belonging to different irreducible representations, we get a factoring of the secular equation which determines the eigenvectors $\bar{Q}_K$ by using the proper symmetry coordinates, which is just as powerful as the factoring of the MO secular equations by use of symmetry orbitals.

Example: H_2O. To illustrate these principles, we consider the water molecule, which belongs to C_{2v}. The character table is:

C_{2v}				E	C_2	σ_v	σ_v'
x^2, y^2, z^2		z	A_1	1	1	1	1
xy	R_z		A_2	1	1	−1	−1
xz	R_y	x	B_1	1	−1	1	−1
yz	R_x	y	B_2	1	−1	−1	1
			Γ	9	−1	3	1

We take σ_v to be reflection in the plane of the molecule and σ_v' to be reflection in the perpendicular plane bisecting the HOH bond angle. The C_2 axis is

z, and the y axis is perpendicular to the plane of the molecule. Th nine-dimensional representation has been called Γ, and its character i at the bottom. This character is worked out by consideration of th formation of the nine cartesian unit vectors with origins on the three in a way familiar from our consideration of π and σ bonds. Knowl character, we see that

$$\Gamma = 3A_1 + A_2 + 3B_1 + 2B_2$$

The three translational modes account for the representations of x, z, namely, $A_1 + B_1 + B_2$. The three rotations take out $A_2 + B_1$ This leaves only

$$\Gamma_{\text{vib}} = 2A_1 + B_1$$

Thus the three normal modes are all nondegenerate.

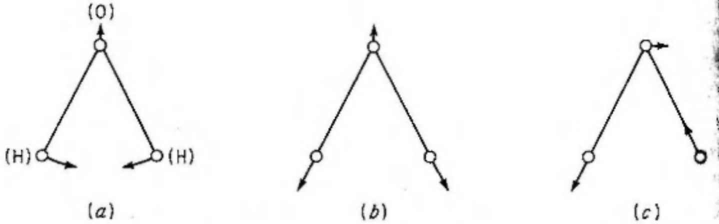

Fig. 7-8. *Normal modes of water molecule.* (*a*)-(*b*) *Symmetry* A_1; (*c*) *symmetry*

The two modes having symmetry A_1 must leave the molecular symm undiminished, since A_1 is the totally symmetric representation. In term internal coordinates, this restricts the motion to a combination of a ch in the bond angle φ and an equal stretch of both OH bond lengths R_1 R_2. These motions are indicated in Fig. 7-8(*a* and *b*). The actual nor coordinates will be two particular linear combinations of the type $Q_K(A_1)$ $a_K\ \delta\varphi + b_K(\delta R_1 + \delta R_2)$. To get the coefficients a and b, a 2×2 secu equation must be solved. From the character table we see that the mode must reduce the symmetry in a way which is odd under C_2 and This is satisfied if we choose $Q(B_1) - c(\delta R_1 - \delta R_2)$. Such a mode is in cated in Fig. 7-8*c*. Actually all these descriptions of the Q's are approxima since we have treated the oxygen atom as infinitely massive. Since it ha finite mass, it will have to move in such a way as to hold the center of m stationary and to eliminate any overall rotation.

Example: C_2H_2. As a second illustration we consider the acetyle molecule, C_2H_2. This is a linear molecule belonging to $D_{\infty h}$. Since it linear, there are only two rotational degrees of freedom. This leav $3N - 5 = 7$ vibrational degrees of freedom. Analysis of the sort indicat for H_2O shows that the vibrational motions decompose as

$$\Gamma_{\text{vib}} = 2\,\Sigma_g^+ + \Sigma_u^+ + \Pi_g + \Pi_u \tag{7-6}$$

two Σ_g^+ modes will preserve the full symmetry of the molecule. The $^+$ mode must be odd under inversion or σ_h but still preserve axial symmetry. Π modes must involve displacements perpendicular to the axis to trans-m suitably for Π representations. The two degenerate modes in each r to vibrations in perpendicular planes through the internuclear axis. ppropriate vibrational configurations are sketched in Fig. 7-9.

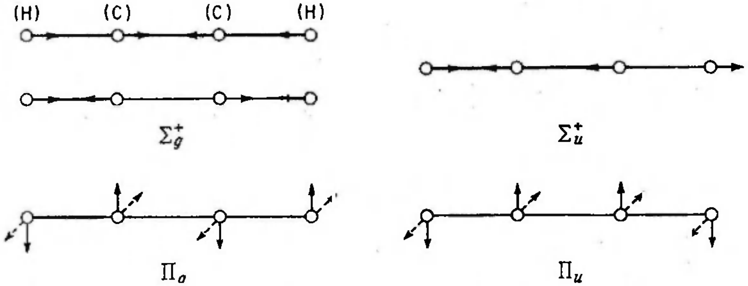

Fig. 7-9. *Normal modes of acetylene molecule. The dashed arrows for the* Π *modes indicate modes degenerate with those shown by solid arrows.*

Combination and overtone levels. Although primary interest is attached to the fundamental absorption in which one mode becomes singly excited, there is also considerable interest in absorptions involving *combination* and *overtone* levels. A combination level is one in which two or more modes of different frequency are excited out of the ground state, whereas an overtone level is one in which there is more than one unit of excitation of a given frequency but none in modes of other frequencies. We start by considering the symmetry of these types of excited states.

As a first example, let us consider the case of a binary combination level in which $v_L = v_M = 1$, all other v_K being zero. From (7-61) we see that the symmetry of the wavefunction is that of $Q_L Q_M$, since $H_1(Q_K) \sim Q_K$, while $H_0(Q_K) = \text{const}$, and the exponential is invariant under all group operations, since it has the same form as the potential energy. But $Q_L Q_M$ is part of the basis of the direct product of the representations to which Q_L and Q_M, respectively, belong. Thus the combination level has symmetry Γ determined by

$$\Gamma = \Gamma(L) \times \Gamma(M) \tag{7-70}$$

If Q_L and Q_M are both nondegenerate, we can find the symmetry of the resulting nondegenerate combination level by identifying the character $\chi = \chi^{(L)}\chi^{(M)}$ in the table. If Q_L and/or Q_M is degenerate, then the decomposition of the direct product into irreducible representations gives us information about the degeneracy as well as the symmetry of the combination level. For example, if a twofold and a threefold level are singly excited, the total degeneracy is 6. However, when account is taken of the anharm coupling terms, this degeneracy will be broken down as determined b dimensionality of the irreducible representations found in the direct pro For the specific example of acetylene, treated earlier, if there is single e tion of both the Π_u and Π_g modes, one finds

$$\Pi_u \times \Pi_g = \Sigma_u^+ + \Sigma_u^- + \Delta_u \qquad (7$$

Thus, when account is taken of anharmonic coupling, this fourfold degen level will split into two nondegenerate levels and one doubly degene level. In the general case where more than two modes are excited, method obviously generalizes to the rule that one finds the resulting symm by analyzing the direct product of all the excited Q_K.

Now, if any level is excited to $v_K > 1$, we have to deal with overtone le For simplicity, we initially restrict our attention to the case in which o modes of one frequency are excited. If this frequency is nondegener the situation is very straightforward. As noted earlier, for nondegene modes $P_R Q_K = \pm Q_K$. Thus all characters consist of $\chi^{(K)}(R) = \pm 1$. either case, $P_R Q_K^2 = Q_K^2$, and a similar result holds for all even pow Also, $P_R Q_K^\nu = \chi^{(K)}(R) Q_K^\nu$ for all odd values of ν. Since the Herm polynomial H_{v_K} consists entirely of even powers of Q_K if v_K is even entirely of odd powers if v_K is odd, it follows that all even overtone le belong to the totally symmetric representation, whereas all odd overt levels belong to the same representation as Q_K, namely, that of the f excited level.

Passing now to the case of overtones of degenerate frequencies, encounter a more complex situation. We note first that a simple combi tional argument shows that the degeneracy of an overtone level is

$$\binom{v+n-1}{v} = \frac{(v+n-1)!}{v\,(n-1)!}$$

where n is the degeneracy of the mode and v is the total number of quanta excitation. For a doubly degenerate frequency, this reduces to simp $(v+1)$, whereas for a triply degenerate frequency it reduces to

$$(v+1)(v+2)/2.$$

As an example, consider a triply excited level of a doubly degenerate mo The $(v+1) = 4$ possible wavefunctions may be written (apart from i variant factors as)

$$\begin{aligned}
\psi_{30} &\sim H_3(Q_{K1}) \\
\psi_{21} &\sim H_2(Q_{K1})H_1(Q_{K2}) \\
\psi_{12} &\sim H_1(Q_{K1})H_2(Q_{K2}) \\
\psi_{03} &\sim H_3(Q_{K2}) \qquad (7\text{-}7
\end{aligned}$$

where Q_{K1} and Q_{K2} are the two degenerate normal coordinates with frequency ω_K. Since these four functions form the complete set of degenerate functions, they must form a basis for a representation of the symmetry group. To determine whether this representation is reducible and, if so, how it reduces, we need to find only its character. This process is simplified by noting that, barring accidental degeneracy, Q_{K1} and Q_{K2} must belong to the same representation, since they are degenerate. Next we note that each of the four functions in (7-72) contains a cubic term and a linear term in the Q's. Since the coordinate transformations R of the symmetry group are linear, the cubic terms themselves must form the basis for a four-dimensional representation. (The linear terms form only a two-dimensional one.) Since the character of a representation is invariant under orthogonal linear transformations of the basis functions, we can for convenience choose Q_{K1} and Q_{K2} for each operator R so that the matrix of R is diagonal. In this case, $Q_{K1} \rightarrow R_1Q_{K1}$ and $Q_{K2} \rightarrow R_2Q_{K2}$ under R, and $\chi_1(R) = R_1 + R_2$. Accordingly, the character of the representation based on Q_{K1}^3, $Q_{K1}^2Q_{K2}$, $Q_{K1}Q_{K2}^2$, Q_{K2}^3 will be

$$\chi_3(R) = R_1^3 + R_1^2R_2 + R_1R_2^2 + R_2^3 \qquad (7\text{-}73)$$

Similarly, the character of the three-dimensional representation corresponding to $v = 2$ will be

$$\chi_2(R) = R_1^2 + R_1R_2 + R_2^2 \qquad (7\text{-}74)$$

and the character in the original two-dimensional representation of R^ν will be

$$\chi_1(R^\nu) = R_1^\nu + R_2^\nu \qquad (7\text{-}75)$$

where ν is any integer. Combining the relations (7-73) to (7-75), we can obtain a result entirely in terms of characters, which will be independent of basis choice, namely,

$$\chi_3(R) = \tfrac{1}{2}[\chi_1(R)\chi_2(R) + \chi_1(R^3)] \qquad (7\text{-}76)$$

This equation can be generalized to

$$\chi_v(R) = \tfrac{1}{2}[\chi_1(R)\chi_{v-1}(R) + \chi_1(R^v)] \qquad (7\text{-}77)$$

which, by iteration, may be used to find the character of any overtone of a doubly degenerate mode. A similar expression can be derived for the case of triply degenerate modes, and explicit (noniterative) expressions can also be derived for both these cases.[1]

To return to the specific example of acetylene, treated earlier, if the Π_g mode is doubly excited, we have

$$\chi_2(R) = \tfrac{1}{2}[\chi_1^2(R) + \chi_1(R^2)] \qquad (7\text{-}78)$$

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[1] See, for example, Wilson, Decius, and Cross, *op. cit.*, chap. 7 and app. XIV.

Noting that $C_\varphi{}^2 = C_{2\varphi}$ and that $\sigma_v{}^2 = E$, etc., one can readily
$\chi_2(R)$ by this formula. Then, by the standard decomposition fo
by inspection, one finds

$$(\Pi_g)^2 = \Sigma_g{}^+ + \Delta_g$$

Thus, with anharmonicity allowed for, this overtone level can spli
twofold degenerate Δ_g level and a nondegenerate $\Sigma_g{}^+$ level.

By combining the results of the specialized cases considered in t
tion, we are now able to work out the symmetry of the most gener
tional level. The general rule is that

$$\Gamma = [\Gamma(1)]^{v_1} \times [\Gamma(2)]^{v_2} \times \cdots \qquad \blacktriangleright$$

where the product runs over all distinct vibrational frequencies and $[\Gamma($
refers to the symmetry of the v_K overtone of the vibration of frequenc
as we have just treated it. In interpreting (7-80), one must of course b
mind that

$$[\Gamma(K)]^2 \neq \Gamma(K) \times \Gamma(K) \qquad \text{(}$$

as is illustrated by (7-79), since $\Pi_g \times \Pi_g = \Sigma_g{}^+ + \Sigma_g{}^- + \Delta_g$, which is
the same as $(\Pi_g)^2 = \Sigma_g{}^+ + \Delta_g$.

7-13 Selection Rules for Vibrational Transitions

As long as we confine our attention to electric-dipole transitions (i.e., th
which are "infrared active"), the selection rules are determined by the ma
element

$$(v_1' \cdots v_{3N}' \,|\sum_\alpha e_\alpha \mathbf{R}_\alpha|\, v_1 \cdots v_{3N}) \qquad \text{(7-}$$

where the e_α are effective charges of the atoms at $\mathbf{R}_\alpha$. Translational a
rotational degrees of freedom being neglected, the indicated eigenfunctio
are of the form (7-61), namely,

$$|v_1 \cdots v_{3N}) = \exp\left(-\tfrac{1}{2} \sum_K \alpha_K{}^2 Q_K{}^2\right) \prod_K H_{v_K}(\alpha_K Q_K) \qquad \text{(7-8}$$

As pointed out earlier, the exponential is invariant under any symmet
operation, since it has the same form as the potential energy. Therefo
the transformation properties are determined solely by the product o
Hermite polynomials. Since we are frequently interested only in th
"fundamental absorption" from the ground state (all $v_K = 0$) to an excite
state in which one mode has been excited to $v_{K'} = 1$, we first simplify to
that case. From the form of the Hermite polynomials, we know that
$H_0(x)$ is a constant and $H_1(x)$ is proportional to x. Thus the ground state
$|0 \cdots 0)$ transforms as the identical representation Γ_1, and the excited state
$|0 \cdots 010 \cdots 0)$ transforms as $Q_{K'}$. Applying our general selection-rule

on, we conclude that normal mode $Q_{K'}$ can be excited from the ground by a dipole transition only if $\Gamma(Q_{K'})$ is included in the irreducible entations $\Gamma(\mathbf{r})$ based on x, y, or z.

In molecular spectroscopy one is also interested in *Raman transitions.* here a quantum of the applied frequency ν is absorbed, and another is ited with frequency $\nu \pm \nu_{ab}$, where $h\nu_{ab} = E_a - E_b$ is the difference in rgy of two states of the system. The frequency of the Raman scattered iation is $(\nu - \nu_{ab})$ or $(\nu + \nu_{ab})$, depending on whether the incident radiation uses a transition from state b to a, or vice versa. For historical reasons, he two possibilities are called "Stokes" and "anti-Stokes" transitions, pectively. Evidently, Stokes transitions will dominate when $h\nu_{ab} \gg kT$. tailed quantum-mechanical investigation shows that Raman transitions n occur only if dipole matrix elements exist between both states a and b d some intermediate state i. But if $(a|\mathbf{r}|i) \times (i|\mathbf{r}|b) \neq 0$, then under ll conditions of interest, $(a|\mathbf{rr}|b) \neq 0$, where $\mathbf{rr}$ includes all bilinear forms in he coordinates. From this loose argument we conclude that Raman excitation by a Stokes transition is possible for modes such that $\Gamma(Q_K)$ is included in the representations of the bilinear terms x^2, y^2, z^2, xy, yz, zx. The same conclusion is reached by imagining the process to go in two steps: the absorption of the initial photon must take the system to a state i of a representation found in $\Gamma(\mathbf{r})$. The emission of the scattered photon then takes the system from i to a state found in $\Gamma(\mathbf{r}) \times \Gamma(\mathbf{r})$, by the selection-rule theorem. But

$$\Gamma(\mathbf{r}) \times \Gamma(\mathbf{r}) = \Gamma(x^2) + \Gamma(y^2) + \Gamma(z^2) + \Gamma(xy) + \Gamma(yz) + \Gamma(zx).$$

Therefore the overall transition is governed by the transformation properties of these bilinear terms.

In working out selection rules for more general transitions involving combination and overtone levels, the overall symmetry as given by (7-80) must be used. That is, ordinary dipole transitions between states a and b are not forbidden by symmetry if Γ_b is found in the direct product $\Gamma(\mathbf{r}) \times \Gamma_a$. Similarly, Raman transitions are not forbidden if Γ_b is found in $\Gamma(\mathbf{rr}) \times \Gamma_a$.

Note that the Raman-transition operators have even parity, while the direct dipole operator has odd parity. Therefore, in molecules with a center of symmetry, in which therefore parity is a good quantum number for the irreducible representations of the vibrational modes, the same vibrational frequency cannot appear in both the direct and Raman spectra. This important principle is often referred to as the *exclusion rule* of molecular spectra.

We now illustrate these principles by considering the molecular examples treated earlier.

$H_2O(C_{2v})$ ■ Here $\Gamma(z) = \Gamma(x^2) = \Gamma(y^2) = \Gamma(z^2) = A_1$ and $\Gamma(x) = \Gamma(xz) = B_1$. Therefore all the vibrational modes can be excited from the ground state by either direct or Raman transitions.

$C_2H_2(D_{\infty h})$ ■ Here $\Gamma(x^2+y^2)=\Gamma(z^2)=\Sigma_g^+, \Gamma(z)=\Sigma_u^+, \Gamma(xz$ Π_g, and $\Gamma(x, y)=\Pi_u$. Therefore only the Σ_u^+ and Π_u modes can be d excited, whereas only the Σ_g^+ and Π_g modes can be excited in a transition. Actually, the infrared active modes can be picked out by i tion of the sketches in Figs. 7-8 and 7-9 showing the vibrational mo The infrared active modes are those with an overall oscillating dipole mo allowing for equivalence of symmetrically related atoms. A less o example is the question of whether or not a dipole transition betwe overtone level $(\Pi_g)^2$ and the combination level $\Pi_g\Pi_u$ is allowed by symm The decompositions of these two levels are $(\Sigma_g^+ + \Delta_g)$ and $(\Sigma_u^- + \Sigma_u^+ +$ as found previously. Because of the parity change, only a direct tran is possible. Inspection of the character tables shows that the x and y c ponents can do nothing but that the z component of the dipole moment couple $\Sigma_g^+ \leftrightarrow \Sigma_u^+$ and $\Delta_g \leftrightarrow \Delta_u$. Thus, transitions between these pai sublevels can in principle occur. They would be expected to be very compared with the fundamental absorptions, however.

7-14 Molecular Rotation

We now proceed to the next smaller term in the molecular Hamilton This is the energy associated with the rotational degrees of freedom. characteristic rotational energies are typically of the order of a few re rocal centimeters, whereas the vibrational energies were usually of the or of 1,000 cm^{-1}. The rotational degrees of freedom are to a good approxi tion independent of the electronic and vibrational ones. We may sim average over those relatively rapid internal motions and treat the molecu rotation as that of a rigid body. The errors introduced by this *rigid-ro* approximation can then be handled by small correction terms for c trifugal stretching and for electron "slip."

The rotational properties of a rigid body are completely specified by three principal moments of inertia $I_a \leqq I_b \leqq I_c$, which lie on princi axes fixed in the molecule. In terms of these, the Hamiltonian is

$$H=\frac{J_x^2}{2I_x}+\frac{J_y^2}{2I_y}+\frac{J_z^2}{2I_z}$$

▶ (7-8

where the association between a, b, c and x, y, z is left free for convenien Thus we need only calculate matrix elements of J_x^2, J_y^2, and J_z^2 with resp to axes gyrating with the molecule. This is readily done after we note th the commutation relations for angular momenta referred to *gyrating* ax have a *reversed* sign, namely,

$$J_xJ_y - J_yJ_x = -i\hbar J_z$$

▶ (7-8

d cyclic permutations. This sign change is equivalent to a reversal of order of the successive operations in the left member, which corresponds the fact that the successive operations are now to be carried out with pect to rotated axes (see Sec. 5-3). When matrix elements are worked ut with the sign change, the major difference is that

$$J^+ = J_x + iJ_y$$

now a *lowering* operator, rather than a raising operator. To distinguish the two coordinate systems, we introduce the following notation: We Write J^+ instead of J_+ to indicate that we are in the gyrating system. Also, we use $g = x, y, z$ for gyrating axes and $F = X, Y, Z$ for space-fixed axes. Finally, we introduce the quantum number K for J_z, retaining M for J_Z.

The basic matrix elements are found to be ($\hbar$ being suppressed throughout)

$$(JK|\,J_z\,|JK) = K \tag{7-86a}$$

$$(JK \mp 1|\,J^\pm\,|JK) = [J(J+1) - K(K \mp 1)]^{\frac{1}{2}} \tag{7-86b}$$

Using these, we can work out the necessary matrix elements by matrix multiplication. We find the diagonal elements to be

$$(JK|\,J_x^2\,|JK) = (JK|\,J_y^2\,|JK) = \frac{J(J+1) - K^2}{2} \tag{7-87a}$$

$$(JK|\,J_z^2\,|JK) = K^2 \tag{7-87b}$$

so that $J_x^2 + J_y^2 + J_z^2 = J(J+1)$, as must hold for a diagonal element. The off-diagonal elements are

$$\begin{aligned}(J, K \pm 2|\,J_x^2\,|JK) &= -(J, K \pm 2|\,J_y^2\,|JK)\\ &= \tfrac{1}{4}[J(J+1) - K(K \pm 1)]^{\frac{1}{2}}[J(J+1) - (K \pm 1)(K \pm 2)]^{\frac{1}{2}}\end{aligned} \tag{7-88}$$

Therefore the only nonvanishing matrix elements of the Hamiltonian are

$$(JK|\,H\,|JK) = \frac{1}{4}\left(\frac{1}{I_x} + \frac{1}{I_y}\right)[J(J+1) - K^2] + \frac{1}{2I_z}K^2 \tag{7-89a}$$

and

$$\begin{aligned}(J, K \pm 2|\,H\,|JK) &= \frac{1}{8}\left(\frac{1}{I_x} - \frac{1}{I_y}\right)[J(J+1) - K(K \pm 1)]^{\frac{1}{2}}\\ &\quad \times [J(J+1) - (K \pm 1)(K \pm 2)]^{\frac{1}{2}}\end{aligned} \tag{7-89b}$$

Symmetric top. Before approaching this general Hamiltonian, let us consider the important special case where two of the moments of inertia, I_x and I_y, are equal. Then the $(K \pm 2|\,H\,|K)$ elements [(7-89*b*)] vanish, and the Hamiltonian is exactly diagonal in our representation based eigenstates. We can simply read off the energy levels from (7-89*a*),

$$
\begin{aligned}
E(K, J) &= \frac{1}{2I_x}\,[J(J+1) - K^2] + \frac{1}{2I_z}\,K^2 \\
&= BJ(J+1) + (A - B)K^2
\end{aligned}
$$

where *A* and *B* are conventional symbols for half the reciprocal mo of inertia. The result (7-90) is almost obvious by inspection of the H tonian, since $K^2 = J_z^2$ and $J(J+1) - K^2$ must then be $J_x^2 + J_y^2$. We that these levels (except $K = 0$) are doubly degenerate. The values $\pm\,|K|$ have the same energy and correspond simply to rotation in opp senses about the figure axis.

In the still simpler case of the linear molecule, $I_z = 0$. Therefore only states with finite energy have $K = 0$, and the energy becomes

$$E(J) = \frac{1}{2I}\,J(J+1) = BJ(J+1) \qquad (7\text{-}$$

Selection rules and spectrum. By symmetry the permanent electric-dip moment of a symmetric top molecule must lie along the figure or *z* a Therefore it transforms as the *z* component of a vector operator. By Wigner-Eckart theorem this leads to selection rules for pure rotational tran tions requiring that

$$\Delta J = \pm 1, 0 \qquad \Delta K = 0 \qquad (7\text{-}9$$

Since *K* does not change in a transition, the energy difference for a tran tion from *J* to *J* + 1 is simply

$$h\nu = B[(J+1)(J+2) - J(J+1)] = 2B(J+1) \qquad (7\text{-}9$$

Thus, just as in the Landé interval rule for atomic fine structure, the lev separation is proportional to the higher of the two angular momenta involve in the transition. Since $J = 0, 1, 2, \ldots$, this formula predicts that succes sive rotational-transition frequencies should be harmonics of the lowes frequency. This rule is excellently obeyed in practice, as is verified by ver precise microwave spectroscopy. The main departures arise from centri fugal distortion, which can be viewed as a change in I_x resulting from the stretching of the molecule by the centrifugal force as one goes to highe rotational levels.

7-15 Effect of Nuclear Statistics on Molecular Rotation

The simple results indicated above need to be modified slightly when the molecule under consideration contains identical nuclei. In that case, the ement of the molecule by a classical rigid body is not completely justi-. The reason for this is that a rotational motion of the molecule effec- y interchanges nuclei. If nuclei are identical, the total wavefunction t be either symmetric or antisymmetric under such an interchange, nding on whether the nuclei involved are bosons or fermions. This uirement may eliminate certain rotational-energy levels or at least change tistical weights because of the nuclear spin degrees of freedom.

We shall confine our attention to the simple and important case of monuclear diatomic molecules.[1] In this case there are just two nuclei to nsider. We can interchange the nuclei, while restoring everything else its original position, by the following series of operations:

1. Rotate the entire molecule through an angle π.
2. Invert the electrons back through the center of symmetry.
3. Reflect the electrons in a plane through the molecular axis perpendicular to the axis of rotation.

The rotation 1 introduces a ± sign depending on whether the rotational ngular momentum J or $\mathscr{K}$ is $\begin{pmatrix}\text{even}\\ \text{odd}\end{pmatrix}$. (The notation $\mathscr{K}$ is used if the total angular momentum J also contains a spin part.) Operation 2 introduces a ± sign for $\begin{pmatrix}g\\ u\end{pmatrix}$ states. For $\Sigma^{\pm}$ states, operation 3 introduces a ±. For $\Pi, \Delta, \ldots$ states, the twofold degeneracy of $\Lambda = \pm|\Lambda|$ is slightly split by the presence of rotation, a phenomenon known as Λ doubling. The appropriate eigenfunctions[2] in the presence of rotation are $(F_+e^{i|\Lambda|\varphi} \pm F_-e^{-i|\Lambda|\varphi})$, where F_+ and F_- are functions independent of φ, variation of φ representing a rotation of the entire electron cloud about the molecular axis. In this case, one can show that one of these combinations is odd and the other is even, so that both signs are available. The overall sign change coming from the product of the three operations above with that from the nuclear wavefunction itself must be ± depending on whether we are dealing with $\begin{pmatrix}\text{bosons}\\ \text{fermions}\end{pmatrix}$.

Examples. O_2^{16} ■ $^3\Sigma_g^-$. $I = 0$. Since there is electronic-spin angular momentum, we denote the rotational quantum number by $\mathscr{K}$ (so that $\mathbf{J} = \mathscr{K} + \mathbf{S}$). Then the operations 1, 2, and 3 introduce sign changes as follows:

$$(-1)^{\mathscr{K}}(+1)(-1) = (-1)^{\mathscr{K}+1}$$

---

[1] For the more general case, see, for example, C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," pp. 69 and 102, McGraw-Hill Book Company, Inc., New York, 1955.

[2] See, for example, R. de L. Kronig, "Band Spectra and Molecular Structure," pp. 63–65, Cambridge University Press, New York, 1930. Original references are R. de L. Kronig, *Z. Physik*, **46**, 814 (1927), **50**, 347 (1928); E. Wigner and E. E. Witmer, *Z. Physik*, **51**, 859 (1928).

The nuclear wavefunction must be symmetric since only one state is av for $I = 0$, namely, $M_I = 0$. Since the nuclear spin is integral, the are bosons and we must have symmetry (not antisymmetry) under interch Thus we require

$$(-1)^{\mathscr{K}+1} = +1$$

or

$$\mathscr{K} = \text{odd}$$

Thus the only rotational levels of O_2 are $\mathscr{K} = 1, 3, 5, \ldots.$ These re tions naturally disappear if the isotopes are different. Thus $O^{16}O^{17}$ h rotational levels available, including the nonrotating $\mathscr{K} = 0$ state, whi forbidden to O_2^{16}.

H_2 ■ ${}^1\Sigma_g{}^+$, $I = \frac{1}{2}$. Here the first three operations produce $(-1)^{\mathscr{K}}$, the final result must be (-1) since we have Fermi statistics. Therefor nuclear-spin state must be symmetric for odd $\mathscr{K}$ and antisymmetric even $\mathscr{K}$. The symmetric state is the $F = 1$ state, represented by $\alpha(1)$ $[\alpha(1)\beta(2) + \beta(1)\alpha(2)]/\sqrt{2}$, and $\beta(1)\beta(2)$. The antisymmetric state is $F = 0$ state $[\alpha(1)\beta(2) - \beta(1)\alpha(2)]/\sqrt{2}$. Thus the statistical weight of odd-$\mathscr{K}$ levels is three times that of the even-$\mathscr{K}$ levels because of the nuc degeneracy. The more populous levels are called *orthohydrogen*, the l populous *parahydrogen*. Because of the weak coupling between the nucl spins and the rest of the world, the conversion between ortho- and p states is very slow. This can cause anomalous low-temperature spec heats because molecules get "trapped" in the $\mathscr{K} = 1$ state and cann drop readily into the $\mathscr{K} = 0$ ground state.

The ortho-para ratio is given in general by $(I + 1)/I$, as has been illustrat by the results ∞ for $O_2(I = 0)$ and 3 for $H_2(I = \frac{1}{2})$. To see that this rat is generally true, consider the sorts of nuclear-spin functions possible f two nuclei having spin I. Since there are $(2I + 1)$ different m_I values f each, there are $(2I + 1)^2$ possible product functions. Of these, $(2I +$ will have $m_I(1) = m_I(2)$, and hence they must obviously be symmetri The remaining $[(2I + 1)^2 - (2I + 1)]$ functions can be grouped int equal numbers of symmetric and antisymmetric combinations of the so $[m_I(1)m_I'(2) \pm m_I'(1)m_I(2)]$. From this we see that the number of sym metric combinations is $(2I + 1)(I + 1)$, whereas the number of antisym metric combinations is $(2I + 1)I$. Taking the ratio, we have the general resul

$$\frac{\text{Number of symmetric combinations}}{\text{Number of antisymmetric combinations}} = \frac{I + 1}{I} \qquad \text{(7-94}$$

This result may be used to determine a nuclear spin I from the alternatin intensities of lines in molecular band spectra. This method was particularl important in early work, and it is still useful because it works independentl of the magnitude of any nuclear moments. In fact it works best whe

0 so that there can be no hyperfine structure at all. This property es it useful for determining whether the absence of hyperfine structure spectrum is actually due to $I = 0$ or merely to a fortuitously small gnetic moment or quadrupole moment.

16 Asymmetric Rotor

an asymmetric rotor, all three moments of inertia are distinct. In this se, (7-89) shows that we have matrix elements which are off-diagonal in (J) as well as diagonal. However, J is still a rigorous quantum number, as is M $(= J_Z)$, as they must be because of the isotropy of space. Since the energy is independent of M, we can give M any convenient value, such as 0 or J. Thus the overall Hamiltonian matrix for any given M value is composed of $(2J + 1) \times (2J + 1)$ blocks along the diagonal, for $J = 0, 1, 2, \ldots$. There is enough symmetry in the Hamiltonian even here to get some further factoring of the secular equation. First, since the only off-diagonal matrix elements (7-89b) connect states differing by two units in K, each block could be factored into two parts simply by separating the even and odd values of K. Second, inspection of the Hamiltonian matrix elements shows that the matrix is symmetric under reflection across either diagonal—not just across the principal diagonal, as is required for any real Hermitian matrix. This symmetry between $\pm |K|$ arises because of time-reversal symmetry, and it suggests forming the symmetric and antisymmetric combinations $(\psi_K \pm \psi_{-K})/\sqrt{2}$. Since these two types of combinations have distinct symmetries, there are no matrix components of energy between them. The transformation to these symmetrized basis functions is carried out by the Wang symmetrizing transformation.[1]

$$X = X^{-1} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & \sqrt{2} & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 1 \end{pmatrix} \qquad (7\text{-}95)$$

Thus the $(2J + 1) \times (2J + 1)$ submatrix for a given J, after the transforma-

$$H_J' = X_J^{-1} H_J X_J$$

and some reordering of rows and columns to separate even and odd K, is factored into four sub-submatrices, each of dimension approximately $J/2$

---

[1] S. C. Wang, *Phys. Rev.*, **34**, 243 (1929); J. H. Van Vleck, *Phys. Rev.*, **33**, 467 (1929).

instead of $(2J + 1)$. This decrease in order of the secular equations facilitates solution. Townes and Schawlow[1] tabulate the exact al solutions for low-lying levels. When the secular equations becom large for exact algebraic solution, the continued fraction-expansion m gives a rapidly convergent numerical solution.[2] Extensive numerical lations of these rigid-rotor eigenvalues have been compiled by King, H

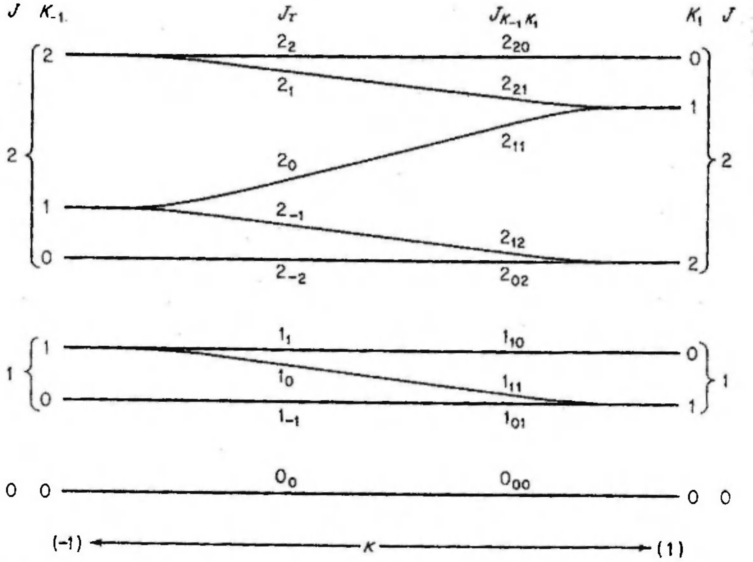

Fig. 7-10. *Qualitative behavior of asymmetric top energy levels showing com notations for labeling of energy levels, as described in the text.*

and Cross.[3] These tables, which are at the heart of much of microwa spectroscopy, are reproduced in the appendixes of the books of Strandb and of Townes and Schawlow, cited above. They give the energies of low-lying states for a large number of degrees of asymmetry between th prolate and oblate symmetric top.

The degree of asymmetry is an important parameter, since it determin how far the solutions will deviate from the simple symmetric top result The most useful asymmetry parameter is that of Ray[4] which is defined by

$$\kappa = \frac{2B - A - C}{A - C} \qquad (7\text{-}96)$$

---

[1] Townes and Schawlow, *op. cit.*, p. 90.

[2] See, for example, M. W. P. Strandberg, "Microwave Spectroscopy," p. 11, Methuen Co., Ltd., London, 1954.

[3] G. W. King, R. M. Hainer, and P. C. Cross, *J. Chem. Phys.*, **11,** 27 (1943); **17,** 82 (1949).

[4] B. S. Ray, *Z. Physik*, **78,** 74 (1932).

where the three rotational constants are ordered so that $A > B > C$. This gives -1 for a prolate symmetric top ($B = C$) and $+1$ for an oblate symmetric top ($B = A$).

Since K is not a good quantum number in the asymmetric top, an additional label must be introduced to supplement J in denoting a particular level. One system of notation which is used is to give K_{-1} and K_{+1}, the values of K found by letting the asymmetry parameter κ go continuously to -1 and $+1$ from the actual value. Thus the level 4_{32} is one where $J = 4$, $K_{-1} = 3$, and $K_1 = 2$. An alternative notation simply numbers the levels in order of energy with an index $\tau(-J \leqslant \tau \leqslant J)$ so that the J_{-J} level is the lowest and J_J is the highest of the $(2J + 1)$ levels. One can show that $\tau = K_{-1} - K_1$; so there is a simple relation between these nomenclatures. These features are illustrated in Fig. 7-10, which shows qualitatively the dependence of energy levels on asymmetry. The energy levels at both $\kappa = -1$ and $+1$ are easily found from (7-90). When $\kappa \neq \pm 1$, the degeneracy of $\pm K$ levels splits, and since there must be a continuous variation with κ, such a connection diagram results.

7-17 Vibration-Rotation Interaction

So far we have discussed what might be called the zero-order Born-Oppenheimer approximation in which the state of the molecule is described as a simple product of an electronic function computed for clamped nuclei, a vibrational eigenfunction, a rotational eigenfunction, a nuclear-spin eigenfunction, and of course in principle a center-of-mass translational eigenfunction. The total energy is expressed as a sum of contributions from each of these degrees of freedom. However, we know from our derivation of the Born-Oppenheimer separation that there are coupling terms in the Hamiltonian which make the separation only approximate. We shall now take up some of the coupling terms to see what their effect is. First we shall consider the interaction between the vibrational and rotational degrees of freedom.

In our treatment of the rotational energy, we treated the nuclear framework as a rigid body. We now take account of the fact that the nuclei are fixed in place only by the finite restoring forces which describe the vibrational motion. As an example, consider the simple diatomic molecule. We take a Hamiltonian describing both rotation and vibration, including an anharmonic potential of the sort considered in (7-47), namely,

$$H = \frac{1}{2\mu R^2}\mathbf{J}^2 + a_2\xi^2 + a_3\xi^3 + \frac{P^2}{2\mu} \tag{7-97}$$

where, as before, μ is the reduced mass, μR^2 is the moment of inertia, and ξ is a dimensionless vibrational coordinate. Since we no longer treat the molecule as rigid, R cannot be replaced by its equilibrium value culating the moment of inertia. Rather we expand,

$$\frac{1}{R^2} = \frac{1}{R_e^{\,2}}[1 - 2\xi + 3\xi^2 + \cdots] \qquad \xi = \frac{R - R_e}{R_e}$$

Then we rewrite the Hamiltonian as $H = H_0 + H'$, where

$$H_0 = B_e\mathbf{J}^2 + a_2\xi^2 + \frac{p^2}{2\mu}$$

and

$$H' = a_3\xi^3 - 2B_e\xi\mathbf{J}^2 + 3B_e\xi^2\mathbf{J}^2 \qquad ($$

and $B_e = (2\mu R_e^{\,2})^{-1}$. Now, the product of a harmonic-oscillator eige tion of ξ and a rotational eigenfunction corresponding to some J fo eigenfunction for H_0. H' provides the correction terms due to anha city and coupling between rotation and vibration. The matrix eleme H are readily written down in a $|vJM)$ representation. Carrying th turbation theory to second order, and subtracting the vibrational-e terms which we found earlier in the pure vibrational problem [Eq. (7 we obtain

$$W_{\text{rot}} = [B_e - \alpha_e(v + \tfrac{1}{2})]J(J + 1) - DJ^2(J + 1)^2 \qquad ▶ \ (7\text{-}$$

where

$$\alpha_e = -B_e\left[\frac{2a_3\lambda^6}{B_e} + 6\lambda^2\right]$$

$$= -B_e\left[\frac{2a_3B_e^{\,2}}{(\hbar\omega_e)^3} + \frac{6B_e}{\hbar\omega_e}\right] \qquad (7\text{-}10$$

and

$$D = \frac{4B_e^{\,3}}{(\hbar\omega_e)^2} \qquad (7\text{-}10$$

The term in α_e accounts for the fact that vibrational motion gives a va for $\langle 1/R^2\rangle_{\text{av}}$ different from $1/R_e^{\,2}$. Therefore the moment of inertia depen on the amplitude of the vibration. The anharmonic coefficient a_3 is negat and large enough to overcome the second term in (7-100*a*). Therefore is a positive quantity, and the rotational constant $B_v = B_e - \alpha_e(v +$ decreases as one goes to excited vibrational states. Even in the ground sta the zero-point vibration reduces B_0 below the value B_e which it would have the nuclei were at the equilibrium separation giving a minimum of potent energy.

The term $DJ^2(J + 1)^2$ arises from centrifugal distortion. Classically, th centrifugal force is proportional to ω^2 and hence to J^2. This force th produces a proportional increase in R and in the moment of inertia. Th in the corresponding quantum-mechanical result. Perhaps the expression is more easily understood when written as

$$W_{\text{rot}} = B_{vJ}J(J+1) \tag{7-101}$$

$$B_{vJ} = B_e\left[1 - \frac{\alpha_e}{B_e}\left(v + \frac{1}{2}\right) - \frac{D}{B_e}J(J+1)\right] \tag{7-101a}$$

lly shows the effect of vibration and centrifugal distortion on the rotational constant. Note that (7-100*a*) and (7-100*b*) show that both α_e and go to zero if the molecule is made rigid ($\hbar\omega_e \rightarrow \infty$). This is, of course, expected from the physical nature of the effects.

We can readily extend these results from the diatomic case to the case of a polyatomic molecule with three principal reciprocal moments of inertia A, B, C. Since each of $(3N - 6)$ normal modes of vibration will enter in changing these moments, we have

$$\begin{aligned} A_v &= A_e - \sum_{i=1}^{3N-6} \alpha_i^A(v_i + \tfrac{1}{2}) \\ B_v &= B_e - \sum_{i=1}^{3N-6} \alpha_i^B(v_i + \tfrac{1}{2}) \\ C_v &= C_e - \sum_{i=1}^{3N-6} \alpha_i^C(v_i + \tfrac{1}{2}) \end{aligned} \tag{7-102}$$

where each α_i includes anharmonic as well as harmonic effects. The various coefficients can be evaluated experimentally if data are available on enough excited vibrational states.

It is a bit more difficult to take account of centrifugal-distortion effects in the general asymmetric top. For a symmetric top, however, the generalization is simple. Since the energy can depend only on *squares* of angular momenta, we have

$$\begin{aligned} W(J, K) = B_vJ(J+1) &+ (A_v - B_v)K^2 \\ &- D_JJ^2(J+1)^2 - D_{JK}J(J+1)K^2 - D_KK^4 \end{aligned} \tag{7-103}$$

The parameters D_J, D_{JK}, D_K are in principle determined by the values of *A* and *B* and the various vibrational frequencies. However, in practice they are determined by fitting the experimental data. Since microwave spectroscopic data can be fitted to parts per million by such a function, the moments of inertia can be found to a similar accuracy. From these, the structural parameters (bond lengths and angles) may be determined with very high precision since the atomic masses are known from other experiments.

7-18 Rotation-Electronic Coupling

When one takes cognizance of the fact that a molecule consists of
tronic-charge cloud surrounding a nuclear framework which is rot
seems evident that the electronic motion will be perturbed by the r
with observable effects. One simple approach to this problem is to
the nuclei as an infinitely massive classically rotating set of force c
Then the Hamiltonian for the electrons has an explicit time depen
arising from the motion of the nuclei. However, if one transforms
coordinates x_i' measured in the rotating system, the problem look
independent. This suggests seeking a solution to the time-depe
Schrodinger equation, which will look stationary in the moving
Following this approach, one finds that the electrons must satisfy an ef
Hamiltonian given by

$$H_0 - \boldsymbol{\omega} \cdot \mathbf{L} \qquad (7$$

where H_0 is the Hamiltonian in absence of rotation, $\mathbf{L}$ is the electr
orbital angular momentum and $\boldsymbol{\omega}$ is the angular velocity of the mole
framework. This result is equivalent to the Coriolis force of classical m
nics or the effective magnetic field which enters in Larmor's theo
Although (7-104) leads to proper results when we replace $\boldsymbol{\omega}$ by $\mathbf{J}/I =$
and treat the rotation quantum mechanically, there remain some quest
which can be clarified by a unified approach in which a single overall Ha
tonian is used throughout.

This overall Hamiltonian contains the energy of the electrons and t
of the rotating nuclei. If we consider the Hamiltonian of the electro
referred to a cartesian-coordinate system fixed in the rotating frame, it
retain exactly the same form as before, namely $H_0 = \sum_i \mathbf{p}_i^2/2m + V$.
this, $p_i = \partial T/\partial \dot{q}_i$, which turns out to be mv_i, where v_i is measured in the *fix*
frame. Thus the form of the Hamiltonian stays the same, as opposed
the result (7-104), which is based on a different viewpoint. The rotation
energy of the bare nuclear framework will be given by

$$H_{\text{rot}} = \sum_g B_g N_g^2 = \sum_g B_g (J_g - L_g)^2 \qquad (7\text{-}10$$

where g runs over the three principal axes in the gyrating system, N_g is th
angular momentum of the nuclear frame, L_g is that of the electrons, and
is that of the total system. (For the present, we assume that $S = 0$, re
stricting attention to singlet states.) Of these, only J is a good quantum
number, because the interaction between $\mathbf{L}$ and $\mathbf{N}$ spoils their individua
conservation. Upon restricting attention to a linear molecule, with $B_x =$
$B_y = B_N$ and $B_z = \infty$, and including the electronic Hamiltonian H_0, (7-105)

---

[1] G. C. Wick, *Phys. Rev.*, 73, 51 (1948).

$$\begin{aligned} H &= H_0 + H_{\mathrm{rot}} \\ &= H_0 + B_N[(J_x^2 + J_y^2) - 2(J_xL_x + J_yL_y) + (L_x^2 + L_y^2)] \qquad (7\text{-}106) \end{aligned}$$

note immediately that the cross term exactly reproduces the correction found in (7-104); so the two approaches are equivalent. Since last term in (7-106) is small and essentially independent of rotation, it be dropped in our subsequent discussion. We now briefly consider eral observable effects arising from the cross term in (7-106).

Λ doubling. After dropping the $(L_x^2 + L_y^2)$ term, (7-106) becomes

$$H = H_0 + B_N[(J_x^2 + J_y^2) - 2(J_xL_x + J_yL_y)]$$

nce $\mathbf{J}^2$ and J_z are diagonal operators in a linear molecule, this can be itten as

$$H = H_0 + B_N[J(J+1) - J_z^2] - 2B_N(J_xL_x + J_yL_y] \qquad (7\text{-}107)$$

ince N_z must equal zero in a linear molecule, $J_z = L_z$, which has the quanzed value Λ. Thus the zero-order energy expression is

$$E(n, J, \Lambda) = E_e(n, \Lambda) + B_N[J(J+1) - \Lambda^2] \qquad (7\text{-}108)$$

Where n symbolizes any additional quantum numbers required to specify the electronic state of the molecule. This expression displays the usual twofold degeneracy between states with $\Lambda = \pm|\Lambda|$. When the cross term in (7-107) is introduced as a perturbation, this degeneracy is lifted because it has matrix elements with selection rule $\Delta\Lambda = \pm 1$. In the simple case of a Π state, where $\Lambda = \pm 1$, the two degenerate states are coupled via Σ states $(\Lambda = 0)$. By applying perturbation theory, it is clear that the splitting will be of order

$$\frac{B_N^2 J(J+1)}{h\nu_{\Pi\Sigma}}$$

where $h\nu_{\Pi\Sigma}$ is a typical electronic-energy separation from the Π state of interest to nearby Σ states. Since $h\nu_{\Pi\Sigma} \gg B$, this splitting will be small and we get what is called a *doubling* of the levels. For states with $|\Lambda| > 1$, the splitting is still smaller (usually unobservable), since the perturbation theory must be carried to higher order to obtain an effective matrix element between $+|\Lambda|$ and $-|\Lambda|$. In general, the splitting is of order $B(B/h\nu)^{\Lambda}$.

A crude physical picture of the origin of this doubling results if we consider the effect of the perturbation on the wavefunctions. For $|\Lambda| = 1$, the unperturbed functions have the dependence $e^{\pm i\varphi}$ on angle about the molecular axis. When mixed by the perturbation, these lead to essentially $\cos\varphi$ and $\sin\varphi$ dependences. The resulting electronic-charge distributions have different moments of inertia about the axis of rotation. This leads slightly different rotational constants for the two states, and hence to energy difference proportional to $J(J+1)$.

Electronic contribution to the moment of inertia. The foregoing discuss shows that it is not correct to calculate the molecular moment of iner by assuming the entire atomic mass to be concentrated at the nucleus. is also incorrect to treat the electronic-charge cloud as a rigid body movi with the nuclear framework, because the electrons can "slip" by havi circulating currents within the charge cloud as it rotates. In particular, expect the spherical inner shells of electrons around each nucleus to follo the nuclei, maintaining a fixed orientation in space like the seats on a rotati Ferris wheel. If they do this, slip is complete and these electrons contribu to the moment of inertia exactly as if they were located at the correspondi nucleus. The valence electrons, not being in spherical shells, will tend rotate rigidly with the framework.

To give a more quantitative treatment which still is simple, let us confi our attention to linear molecules in a $^1\Sigma$ ground state. Then we have

$$H = H_0 + B_N J(J+1) + H' \qquad \text{(7-10}$$

where

$$H' = -2B_N(J_x L_x + J_y L_y) \qquad \text{(7-109}$$

Now, when $J \neq 0$, H' will mix some Π states into the Σ state, since L_x a L_y have $\Delta\Lambda = \pm 1$ selection rules. This produces a circulating electron current proportional to $BJ/h\nu_{\Pi\Sigma}$. The effect on the energy appears in secon order perturbation theory as

$$\Delta E = 4B_N^2 J(J+1) \sum_{\Pi} \frac{|(\Pi\,|L_x|\,\Sigma)|^2}{h\nu_{\Pi\Sigma}}$$

where the Σ in the matrix element refers to the ground state and the su runs over all excited Π states. When combined with (7-109), this result show that the effective rotational constant including the electrons is

$$\begin{aligned} B &= B_N + B_e \\ &= B_N - 4B_N^2 \sum_{\Pi} \frac{|(\Pi\,|L_x|\,\Sigma)|^2}{h\nu_{\Pi\Sigma}} \end{aligned} \qquad \text{(7-11}$$

Since the correction term may be of order $10^{-4}B_N$, it must be evaluated befo extremely precise determinations of internuclear distances can be made fro observed values of B. As will now be shown, this correction can be determined from the rotational magnetic moment of the molecule.

Rotational magnetic moment. Since the negative charge in the atoms in molecule is not centered at the nuclei, one would expect a magnetic mome to result from the rotation of even a homonuclear diatomic molecule. Agai however, the circulation produced by the rotation is important. For example, in H_2 the slip is so great that the rotational g factor (defined by $\mu_{\text{rot}} = g_r\beta \mathbf{J}$) is $+0.883\ m/M$ compared with the value $1.00\ m/M$ which would result if there were no electrons at all. [Here m/M is the electronic mass in atomic mass units (amu).] This case is unusual, however, and most molecules will have $g_r < 0$ because the electronic contribution slightly outweighs that of the bare nuclei. The electronic contribution is readily shown to be

$$g_r^e = -4B_N \sum_{\Pi} \frac{|(\Pi\,|L_x|\,\Sigma)|^2}{h\nu_{\Pi\Sigma}} = \frac{B_e}{B_N} \tag{7-111}$$

whereas the nuclear contribution is obviously

$$g_r^n = \frac{Z}{A}\frac{m}{M} \tag{7-112}$$

Since (7-111) shows that the electronic contribution to B can be expressed in terms of the rotational g factor, we can write

$$\begin{aligned} B &= B_N(1 + g_r^e) = B_A(1 + g_r^n)(1 + g_r^e) \\ &\approx B_A(1 + g_r^e + g_r^n) = B_A(1 + g_r) \end{aligned} \tag{7-113}$$

where B_A is the rotational constant calculated by using atomic instead of nuclear masses. Since $|g_r|$ is usually much less than $|g_r^e|$, the use of atomic masses is a good first approximation. However, to determine internuclear distances to the full accuracy of the data, it is necessary to measure g_r experimentally to evaluate the correction. The rotational g factors for a dozen or so molecules have been measured by observing the small Zeeman energy of the rotational magnetic moment in an external field.

Coupling effects of internal magnetic field. The effective magnetic field produced inside a Σ-state molecule by the rotation will give an energetic coupling to the nuclear spins, and to the electronic spin if the molecule is not in a singlet state. These effects are best visualized by considering the rotation to mix in some Π states, which have orbital angular momentum. These then interact with the nuclear moments via the ordinary h.f.s. coupling and with the electron spin via the spin-orbit coupling $\zeta\mathbf{L}\cdot\mathbf{S}$. The former gives rise to an $\mathbf{I}\cdot\mathscr{K}$ term, while the latter gives rise to a term in the effective Hamiltonian having the form

$$\sim \left[\zeta B \sum_{\Pi} \frac{|(\Pi\,|L_x|\,\Sigma)|^2}{h\nu_{\Pi\Sigma}}\right] \mathscr{K}\cdot\mathbf{S} \tag{7-114}$$

where $\mathscr{K} = \mathbf{J} - \mathbf{S}$ is the rotational angular momentum, "high-frequency" effects due to the electronic orbital angular momentum $\mathbf{L}$ being neglected.

It should be clear that various other small correction and spin-coupling terms can arise. The fact that many of them depend on similar sums of squared matrix elements allows a certain amount of interrelation of the d to form a coherent picture of the interaction between rotational and electro degrees of freedom. Examples in which this sort of analysis have b carried particularly far are molecular hydrogen[1] and oxygen.[2]

EXERCISES

7-1 Consider the charge density along the line passing through the nuclei o a hydrogen-molecule ion. Assuming simple LCAO MO's made from ordina atomic hydrogen 1*s* functions, plot the probability density $\rho = |\psi|^2$ for both th ψ_g and ψ_u functions in Eq. (7-11). Note the difference. Compare these with ha the charge density that would result from a classical (i.e., non-wave-mechanica superposition of the charge densities of two hydrogen atoms. Take the int nuclear distance to be 1.06 A = 2.0 atomic units, and the overlap integral S to b 0.586. Note the importance of the overlap correction on the normalization.

7-2 As discussed in the text (Sec. 7-3), the molecular orbital ${}^3\Sigma_g{}^-$ ground sta of O_2 is normally taken to be $(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^2$ outside of filled 1*s* and 2*s* shells If we relax this particular assignment among these three types of orbitals, we hav eight electrons to assign to 10 spin-orbital functions. (*a*) Show that this giv rise to 45 possible Slater determinants. (*b*) Show that there are only three way of assigning electrons to orbitals (with spin unspecified, but obeying the exclusio principle) so as to produce a Σ_g symmetry. (*c*) Taking account of the spin degeneracy, show that these three ways lead to three singlets and two triplets, accountin for a total of 9 of the 45 determinants. (*d*) Considering the triplets, show that both have the symmetry ${}^3\Sigma_g{}^-$. A simple 2 × 2 secular equation would determine the optimum admixture of the two configurations.

7-3 Repeat Exercise 7-2, taking account of the possible occupancy of the $(\sigma_u 2p)$ orbital. This leads to 12 states for the eight electrons. Show that there are now 495 possible determinants, 12 ways of assigning electrons for Σ_g symmetry, 15 singlets, 13 triplets, and 3 quintets, of which there are 9 ${}^3\Sigma_g{}^-$ states. Thus the secular equation for the ground state is only a 9 × 9 after symmetry has been fully utilized to eliminate extraneous determinants from the 495.[3]

7-4 Consider the dominant configuration in O_2, in which the only unfilled shell is the $(\pi_g 2p)^2$ one. (*a*) Considering only these two electrons, show explicitly the different correlations of the azimuthal angles φ_1 and φ_2 of the two electrons in the triplet and singlet spin configurations. (*b*) To allow a rough estimate of the importance of this effect, consider a model in which the electronic wavefunctions are confined to a ring of radius R about the axis of the molecule. Calculate $\langle r_{12}\rangle$ for the singlet and triplet states and for the uncorrelated case of a simple product function (not antisymmetrized). Show that $\langle r_{12}\rangle$ in the singlet and triplet, respectively, are $\frac{14}{15}$ and $\frac{16}{15}$ of $\langle r_{12}\rangle$ for the simple product. Note that, for this model of the wavefunction, $\langle 1/r_{12}\rangle$ would diverge for the singlet and uncorrelated cases, but and for the triplet. This illustrates how the antisymmetry keeps electrons of parallel spin away from each other, with consequent lower electrostatic energy, leading to the Hund rule.

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[1] N. J. Harrick and N. F. Ramsey, *Phys. Rev.*, **88**, 228 (1952).

[2] M. Tinkham and M. W. P. Strandberg, *Phys. Rev.*, **97**, 937 (1955).

[3] See A. Meckler, *J. Chem. Phys.*, **21**, 1750 (1953).

7-5 Consider a hypothetical molecule consisting of three identical atoms arranged at the vertices of an equilateral triangle so that the symmetry of the problem is D_{3h}. (*a*) Find the symmetries of all symmetry orbitals which can be formed from *s* and *p* atomic functions. (*b*) Find linear combinations of atomic functions forming orthonormal basis functions. (*c*) Work out expressions similar to (7-37) for the energies of the orbitals based on the *s* functions.

7-6 Consider the hypothetical triatomic molecule of Exercise 7-5. (*a*) How many vibrational degrees of freedom does it have? (*b*) Find the decomposition of the nine-dimensional representation based on cartesian displacements of the three atoms into irreducible representations of D_{3h}, and identify those corresponding to translation, rotation, and vibration. (*c*) Construct diagrams showing the displacements in each of the vibrational modes. (HINT: Use the basis-function generating machinery, starting with an arbitrary set of displacements having no translational or rotational component.) Which of these modes are infrared-active and which are Raman-active? (*d*) Work out the symmetries and degeneracies of all combination and overtone levels having a total of two units of excitation.

7-7 Consider again the symmetrical triatomic molecule of Exercises 7-5 and 7-6. Let the internuclear distance be a and the mass of each atom be M. (*a*) What are the three principal moments of inertia? (*b*) What are the rotational-energy levels? Make a diagram to scale showing all those for $J \leqq 4$, also indicating the degeneracies for each. (*c*) What transitions, if any, are allowed electric-dipole transitions? Explain.

7-8 Work out general algebraic expressions for all the asymmetric rotor energy levels for $J = 0$, 1, 2, and 3.

7-9 Consider the water molecule H_2O. Let the OH distances be a and the HOH bond angle be θ. (*a*) For general values of these parameters, what are the principal axes and the corresponding moments of inertia? Make a drawing to approximate scale, showing these axes for the actual case of $\theta = 105°$. (*b*) What is the value of Ray's asymmetry parameter κ for a general value θ? (*c*) Using the results of Exercise 7-8, compute the energy levels of H_2O for $J = 0$, 1, and 2. (Use $a = 0.957$ A for the bond length and $\theta = 105°$.) Quote your results in units of reciprocal centimeters. Make an energy-level diagram showing these levels to approximate scale.

7-10 Derive expressions for the vibrational and rotational energy of a diatomic molecule analogous to Eqs. (7-52) and (7-100) but retaining a term $a_4\xi^4$ in the vibrational potential in addition to the terms given in Eq. (7-47).

7-11 In O_2, a $^3\Sigma$ molecule, there is a term of the form $2\lambda S_z^2$, coupling the spin to the molecular figure axis z, and another term, of the form $\mu\mathscr{K}\cdot\mathbf{S}$, where $\mathscr{K}$ is the rotational angular momentum (**J**-**S**), coupling the spin to the rotational motion. [See Exercise 5-10 and Eq. (7-114).] Consider these terms to be added to the usual rotational Hamiltonian $B\mathscr{K}^2$, and solve the resulting Hamiltonian for the energy levels. Note that J and S are good quantum numbers but that $\mathscr{K}$ is not. An exact solution can be obtained for all energy levels, which involves no more than a 2×2 secular equation. Numerical values of the parameters are $B = 1,$ $\lambda = 1.98$, and $\mu = 0.0084\ \text{cm}^{-1}$. [HINT: It is probably easiest to set up the ma elements in a Hund-case (*a*) representation, in which components of the angu momenta along the figure axis are quantized. In this case, the only non component there is $S_z = \Sigma$, since there is no component of the rotational angul momentum of a linear molecule along the axis. Then $S_z^2 = \Sigma^2$, and the ma elements of $\mathbf{J} \cdot \mathbf{S}$ are also readily written down. The Wang transformation (7- applied to the 3×3 matrix for $\Sigma = \pm 1, 0$ will prove useful in reducing the secul equation.[1]]

REFERENCES

COULSON, C. A.: "Valence," Oxford University Press, New York, 1952.

DAUDEL, R., R. LEFEBVRE, and C. MOSER: "Quantum Chemistry," Interscien Publishers, Inc., New York, 1959.

DENNISON, D. M., and K. T. HECHT: Molecular Spectra, chapter in D. R. Bates (ed., "Quantum Theory," vol. II, Academic Press Inc., New York, 1962.

EYRING, H., J. WALTER, and G. F. KIMBALL: "Quantum Chemistry," John Wile & Sons, Inc., New York, 1944.

HEINE, V.: "Group Theory," chap. 5, Pergamon Press, New York, 1960.

HERZBERG, G.: "Molecular Spectra and Molecular Structure," vol. I, 2d ed., Spectr of Diatomic Molecules, vol. II, Infrared and Raman Spectra of Polyatomi Molecules, D. Van Nostrand Company, Inc., Princeton, N.J., 1950, 1945.

PAULING, L., and E. B. WILSON, JR.: "Introduction to Quantum Mechanics," McGraw Hill Book Company, Inc., New York, 1935.

STRANDBERG, M. W. P.: "Microwave Spectroscopy," Methuen & Co., Ltd., London, 1954.

STREITWIESER, A., JR.: "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, 1961.

TOWNES, C. H., and A. L. SCHAWLOW: "Microwave Spectroscopy," McGraw-Hill Book Company, Inc., New York, 1955.

WILSON, E. B., JR., J. C. DECIUS, and P. C. CROSS: "Molecular Vibrations," McGraw- Hill Book Company, Inc., New York, 1955.

[1] See R. Schlapp, *Phys. Rev.*, **51**, 342 (1937); Tinkham and Strandberg, *loc. cit.*

8

SOLID-STATE THEORY

To give any sort of proper coverage to the quantum theory of solids would require much more space than is available here. Rather than trying to survey the entire field in a brief chapter, we shall confine our attention to two aspects which are particularly characteristic of the solid state, namely, the electronic-energy-band structure and the symmetry of magnetic crystals. In our treatments of both of these, we shall find group theory to be a powerful aid.

8-1 Symmetry Properties in Solids

We have already noted that the full symmetry group of a crystalline solid, the space group, contains translational-symmetry operators, rotational-symmetry operators from the point group, and, of course, combinations of the two. The most general space-group element may be represented by t conventional notation $\{\mathbf{R} \mid \mathbf{t}\}$, where $\mathbf{R}$ represents a rotation (proper improper) and $\mathbf{t}$ represents a translation. The corresponding coordin transformation is

$$\mathbf{x}' = \mathbf{R}\mathbf{x} + \mathbf{t} \tag*{(8-}$$

From this property, it is easy to verify that the multiplication rule for tw such operators is

$$\{\mathbf{R} \mid \mathbf{t}\}\{\mathbf{S} \mid \mathbf{t}'\} = \{\mathbf{RS} \mid \mathbf{R}\mathbf{t}' + \mathbf{t}\} \tag*{(8-}$$

Similarly the inverse of $\{\mathbf{R} \mid \mathbf{t}\}$ is given by

$$\{\mathbf{R} \mid \mathbf{t}\}^{-1} = \{\mathbf{R}^{-1} \mid -\mathbf{R}^{-1}\mathbf{t}\} \tag*{(8-}$$

From the forms of these results, it is obvious that the rotational par $\mathbf{R}$ of these operators, obtained by setting $\mathbf{t} = 0$, in themselves form a group This is the point group of the crystal. It is also clear that the pure translation operators $\{\mathbf{E} \mid \mathbf{t}\}$ form a subgroup, one which is both invariant and Abelian. This translational subgroup contains all the translations which can be written in the form

$$\mathbf{t}_n = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \tag*{(8-4)}$$

where n_1, n_2, and n_3 are integers and $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are the three primitive translations which define the periodicity of the lattice. Naturally, these translations are covering operations of the crystal only if it is infinite in extent, or if one neglects surface effects, or if one introduces periodic boundary conditions, so that a finite volume of crystal is imagined to be repeated over and over to fill all space. For many purposes, we can imagine any one of these to be the case with equivalent results. It is usually most convenient to use periodic boundary conditions, and they lead naturally to the running (as opposed to standing) waves which are necessary for treating any electronic transport or conduction process. We shall use them here.

If we ignored all symmetry except the translational symmetry (or if there were no more, as in a triclinic lattice without even inversion symmetry), the entire symmetry classification of an electronic wavefunction in the solid would be given by Bloch's theorem (see Sec. 3-7). The irreducible representations would be completely labeled by giving the *crystal-momentum* quantum number k, defined by the relation (3-26), which in three dimensions becomes

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{a}) = e^{i\mathbf{k}\cdot\mathbf{a}}\psi_{\mathbf{k}}(\mathbf{r}) \tag*{(8-5)}$$

where $\mathbf{a}$ is any of the three primitive translations. Hence, (8-5) also holds when $\mathbf{a}$ is replaced by any $\mathbf{t}_n$ satisfying (8-4). Thus

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{t}_n) = e^{i\mathbf{k}\cdot\mathbf{t}_n}\psi_{\mathbf{k}}(\mathbf{r}) \tag*{▶ (8-6)}$$

As in one dimension, this property allows us to write the most general wavefunction in the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \qquad \blacktriangleright \ (8\text{-}7)$$

where $u_{\mathbf{k}}$ is periodic so that $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{t}_n)$ and $\mathbf{k}$ takes on a discrete set of values determined by the repeat distance in the periodic boundary conditions. Wavefunctions in this Bloch form evidently extend over the entire crystal, representing equal probability that the electron is in any unit cell of the crystal, just as with the plane waves of a completely free electron. Such a form is essential if we are to have a convenient theory of electronic conduction in metals.

If, on the other hand, we ignore the translational symmetry and consider only the point-group symmetry, we are led to the considerations we treated in Chap. 4 in conjunction with the crystal-field-splitting problem. This approach would be justified if the atomic wavefunctions located on the various sites in the crystal had so little overlap or interaction that each atom could be treated separately, with no concern for the existence of other identical atoms in adjacent unit cells in the crystal. In that case, the complete symmetry classification of the wavefunctions is provided by the various irreducible representations of the appropriate point group, namely, that giving the local symmetry about the atomic site. This need not be the same as the point group giving the macroscopic crystal symmetry, also referred to as the *crystal class.*

Our present objective is to bring together the two aspects of the problem mentioned above, so that we can treat the complete symmetry classification of the wavefunctions where both the translational and point-group symmetries have nontrivial consequences. The possibilities for complication as one considers various space groups are so great that we shall severely limit the generality of our discussion so as to illustrate the basic ideas in as simple a way as possible. Thus, we shall largely confine our attention to the 73 *simple*, or *symmorphic*, space groups, in which all symmetry operators which are obtained by taking the direct product of the translational subgroup with the point group are in the space group. In this case, the *entire* point group is a subgroup of the space group. This subgroup is isomorphic to the factor group of the space group with respect to the invariant subgroup of translations. In making this restriction, we exclude the 157 nonsimple space groups, containing glide planes and screw axes. These are elements combining a reflection or rotation with a translation which is *not* of the form (8-4) and accordingly is not separately a group element. For example, when there is a screw diad axis in the symmetry of the system, this means that one symmetry operation of the space group is a rotation by π about an axis, coupled with a translation by half the repeat distance along that axis. In this case, neither the twofold rotation nor the half unit of translation is separately a member of the *space* group. Yet the twofold rotation *is* of the *point* group, as defined above. Thus, in this case, the ent group is *not* a subgroup of the space group. Naturally this leads to what more intricate theory than in the case of the simple space For the requisite generalizations of the treatment given here, the referred to the literature.[1]

8-2 The Reciprocal Lattice and Brillouin Zones

Inspection of (8-6), the relation defining the quantum number, or sentation label, **k**, shows that **k** is actually not uniquely specified. so because if we add any vector **K** to **k**, such that $\mathbf{K}\cdot\mathbf{t}_n$ is a multiple of all $\mathbf{t}_n$, then the defining relation (8-6) is as well satisfied by $\mathbf{k}+\mathbf{K}$ itself. The particular vectors **K** are closely related to the vectors **b** reciprocal lattice, which are defined by the relation

$$\mathbf{b}_1 = \frac{\mathbf{a}_2\times\mathbf{a}_3}{\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)}$$

and two others obtained by cyclic permutation of indices. These have the dimension of reciprocal length and are said to lie in *recip* *space*. We note that in the special case where the three primitive lations in direct space, namely, the $\mathbf{a}_i$, are orthogonal, the $\mathbf{b}_i$ are paral the $\mathbf{a}_i$ and are of length $1/|a_i|$. In any case, it is evident from (8-8) th

$$\mathbf{a}_i\cdot\mathbf{b}_j=\delta_{ij}$$

Thus, if we consider any vector $\mathbf{K}_m$ of the form

$$\mathbf{K}_m = 2\pi(m_1\mathbf{b}_1+m_2\mathbf{b}_2+m_3\mathbf{b}_3) \qquad (8$$

the scalar product $\mathbf{K}_m\cdot\mathbf{t}_n$ will have the value $2\pi(m_1n_1+m_2n_2+$ Since the m_i and n_i are integers, $\mathbf{K}_m\cdot\mathbf{t}_n=2\pi\times$ integer, $e^{i\mathbf{K}_m\cdot\mathbf{t}_n}=1$,

$$e^{i(\mathbf{K}_m+\mathbf{k})\cdot\mathbf{t}_n}=e^{i\mathbf{k}\cdot\mathbf{t}_n} \qquad (8$$

Thus, as far as the defining relation (8-6) is concerned, it is not possibl distinguish between **k** and $\mathbf{k}+\mathbf{K}_m$, where $\mathbf{K}_m$ is given by (8-10), and we consider these as essentially identical **k** values. This shows that we may con all our attention to **k** vectors lying inside a finite zone of this reciprocal sp or **k** space, since any **k** vector lying outside the zone can be considered tical to one inside the zone, by adding a suitable $\mathbf{K}_m$. It is geometric evident that the size of this region is determined by taking that part are closer to the origin than to any of the other reciprocal-lattice points, specified by reciprocal-lattice vectors $\mathbf{K}_m$.[1] This zone may be constructed by setting up perpendicular bisecting planes on the lines connecting the origin to all reciprocal-lattice points and then taking the volume about the origin enclosed by these intersecting planes. The zone constructed in this way is known as the *first Brillouin zone*, and it plays a central role in all our subsequent discussions because all wavefunctions can be classified as having a wave vector $\mathbf{k}$ lying in this zone. In adding or subtracting a $\mathbf{K}$ vector to obtain an equivalent $\mathbf{k}$ vector in the first Brillouin zone, one obtains the so-called "reduced" wave vector. If all wavefunctions are described in terms of such reduced wave vectors, the *reduced-zone scheme* of description results.

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[1] See, for example, G. F. Koster, F. Seitz, and D. Turnbull (eds.), "Solid State Phys vol. V, p. 173, Academic Press Inc., New York, 1957.

On the other hand, in the extended-zone scheme all $\mathbf{k}$ values are considered, and second, third, and higher Brillouin zones are defined to characterize the outlying regions of $\mathbf{k}$ space. The first and second zones for the square lattice are shown in Fig. 8-1, for example. The higher zones all have the same area as the first, and the various pieces of which they consist can be exactly fitted inside the first zone by translation by reciprocal-lattice vectors. The boundaries of all zones are formed by the set of planes described above. The significance of these planes is that, for any $\mathbf{k}$ on one of them, there is another $\mathbf{k}' = \mathbf{k} + \mathbf{K}$ such that $|\mathbf{k}'| = |\mathbf{k}|$. Hence the second wave is degenerate with the first, and, as we shall see directly, first-order shifts in energy can result from the periodic potential. This gives rise to discontinuities in energy along the zone boundaries in an extended-zone description. The extended-zone scheme is particularly useful for nearly free electrons, where the wavefunction is well approximated by a plane wave of some definite $\mathbf{k}$ value, which need not be in the first zone.

As a simple example of these concepts, let us consider a two-dimensional "solid" with a square lattice with primitive translations of length a along both x and y. The reciprocal lattice vectors $\mathbf{b}_i$ then also form a square lattice, with $|\mathbf{b}_i| = 1/a$. In this case the first Brillouin zone is a square, centered on the origin, and extending to $\pm\pi/a$ along both the k_x and k_y directions as shown in Fig. 8-1. Actually, the same information would be contained within any square of the same size, but it is usually most convenient to take the zone centered on the origin. Now, if the periodic boundary conditions require a repetition of the wavefunctions after a displacement by N unit cells along either the x or the y axis, and thus after a distance $L = Na$, the allowed $\mathbf{k}$ values form a discrete set, with both k_x and k_y being restricted to integral multiples of $2\pi/L$ or $2\pi/Na$ (see Sec. 3-7). Thus there are N discrete allowed values of k_x and of k_y, and as a result N^2 values of $\mathbf{k}$, N^2 being

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[1] Strictly speaking, $\mathbf{K}_m/2\pi$ is a reciprocal-lattice vector, since it is composed of integral multiples of the vectors $\mathbf{b}_i$. However, we shall follow conventional usage, which allows the same expression to refer to either one, when there is no danger of confusion.

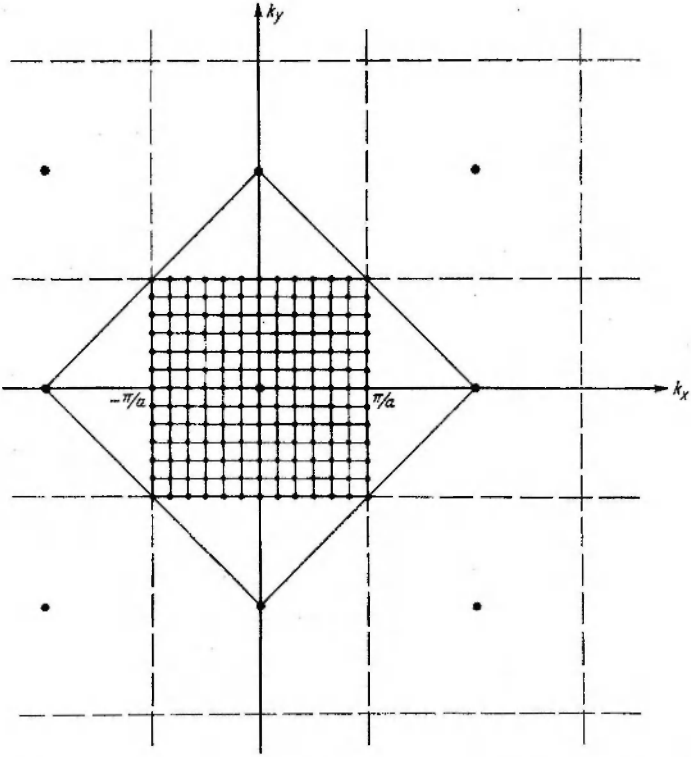


Fig. 8-1. *Schematic diagram of first and second Brillouin zone: The discrete set o allowed k-values is indicated inside the first zone.*

the total number of cells in the coordinate space crystal. This equality i a general result, valid also in three dimensions and independent of the symmetry of the unit cell.

A still simpler example is the one-dimensional case with a period of along the x axis, the example treated explicitly in Sec. 3-7. If the "crystal" is of length $L = Na$, there are N discrete k values, namely, $2\pi p/L$, with being an integer lying between $-N/2$ and $+N/2$, so that k runs from $-\pi/$ to $+\pi/a$. Because we have only a one-dimensional variation of k, we ca now plot the energy of the electronic eigenfunction against k in a simp manner. It is instructive to start out by considering the so-called "empty lattice" case, in which we imagine that the periodic potential associated wit the crystal lattice has been "turned off," leaving the electron free. In th case, we know that the eigenfunctions are plane waves $\psi_k \sim e^{ikx}$ and th corresponding energies are $E_k = \hbar^2k^2/2m$. Although the reciprocal latti should play no substantive role if there is no interaction between the electron and the crystal, we can still use the reduced-zone scheme to plot all energies in a finite range of k values corresponding to the first Brillouin zone. This is illustrated in Fig. 8-2, where the extended-zone scheme is also indicated in a lighter curve. In obtaining the reduced-zone energies, we have simply translated the energy curves by multiples of the reciprocal-lattice distance $2\pi/a$.

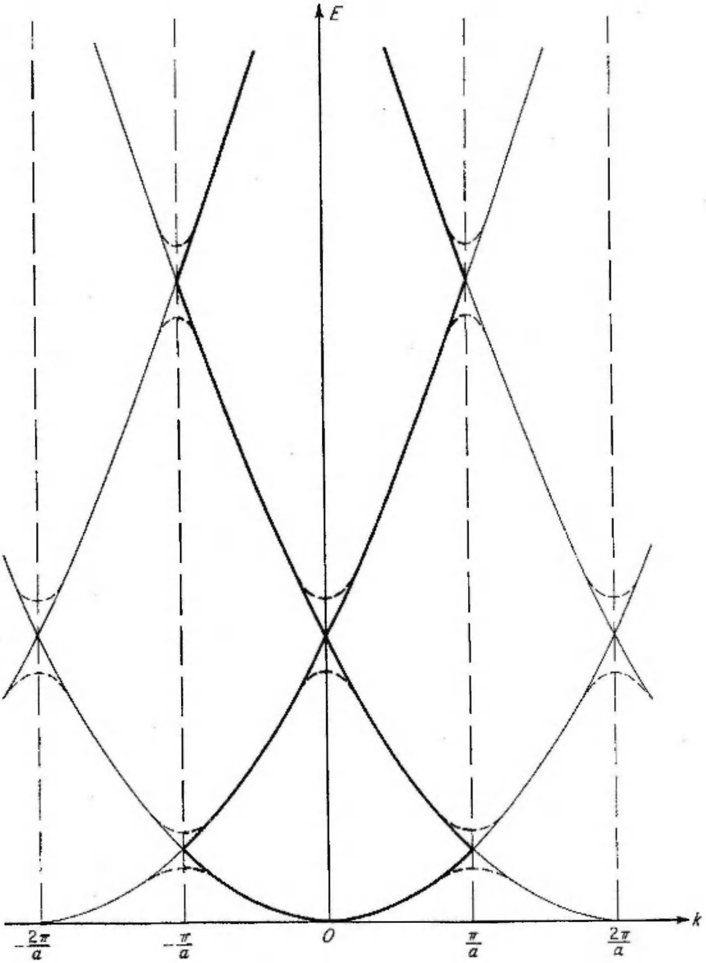


Fig. 8-2. *One-dimensional $E(k)$ curve showing reduced-zone scheme applied to free-electron or empty lattice example. Dotted curves near level crossings represent modifications introduced by finite periodic potential, which results in forbidden bands of energy levels. Recall also that k takes on only a discrete but very finely spaced set of values.*

If we now imagine that the periodic potential of the lattice is turned on but is still weak, then we may consider it as a perturbation on these energy levels. Since by definition the periodic potential $V(x)$ has the periodicity of the lattice, it is invariant under the space group of the crystal, which in this case is simply the cyclic group leading to Bloch's theorem and the classification of representations by k value. Applying the matrix-element theorem (Sec. 4-9), the only matrix elements of $V(x)$ must be those connecting states belonging to the same irreducible representation, hence having the same k value. In other words, the periodic potential couples only states related by a vertical displacement in Fig. 8-2. This results in the usual "repulsion" of energy levels, since the effect of the second-order perturbation will be greatest when the energy denominators are least, namely, near level crossings. This effect is shown schematically by the dotted curves in the figure. The periodic potential thus breaks up the continuum of energy levels for the free electron into a discrete set of bands of allowed energies, separated by forbidden-energy gaps. In the one-dimensional case discussed here, there is no degeneracy except that between k and $-k$. When we consider three-dimensional cases, however, we shall find that there can be many more symmetry-related k values having the same energy and also that there can be several distinct functions having the same k value and the same energy, but distinguished by other symmetry properties. The study of these symmetries and degeneracies will be our main application of group theory in the study of energy bands in solids.

Although we shall not go into it in any detail, it may be appropriate at this point to recall the relation between these electron energy bands and actual observable properties of solids. The central idea is that, because electrons obey Fermi statistics, at absolute zero the energy states of the crystal will be filled with electrons up to an energy level (called the Fermi level) such that all electrons in the system are accounted for. The surface in reciprocal space separating the full from the empty states is called the *Fermi surface*. It will have a symmetry appropriate to the lattice and will not in general be spherical as it is for free electrons. At finite temperatures, electrons will be excited to states within roughly kT of the Fermi energy, resulting in a slight blurring of the surface. (The blurring is slight because $kT \ll E_F = kT_F$, where $T_F \approx 50{,}000°\mathrm{K}$, typically.) Under the influence of a d-c electric field, the only electrons that can respond are those at the Fermi surface, since they can be displaced into an adjacent empty state with slightly different momentum $\hbar k$. If the Fermi energy should fall in the energy gap between two bands, where there is no density of states, such a field can produce no current and we have an insulator. However, if the gap is comparable with kT, there will be some electrons excited above the gap to a *conduction band*, where they are able to be accelerated into empty states, and we have a semiconductor. If the Fermi energy lies within an allowed-energy band, all electrons on the Fermi surface are able to participate in conduction and we have a metal. From this brief sketch it is apparent that a knowledge of the energy-band structure of a solid is fundamental for determining all its electronic properties. Because a straightforward solution is difficult at best, it is worthwhile to draw on group theory for any help symmetry can provide in reducing the magnitude of the problem.

8-3 Form of Energy-band Wavefunctions

It is instructive to carry on this simple one-dimensional example to consider the form of the wavefunctions in the crystal for various k values and various bands. In one dimension, (8-7) becomes simply

$$\psi_k(x) = u_k(x)e^{ikx} \tag{8-12}$$

where $u_k(x + a) = u_k(x)$. Evidently, the entire unsolved problem is reduced to the determination of $u_k(x)$ within one unit cell because the periodicity then determines it over the rest of the crystal.

In the empty-lattice, or free-electron, approximation, we simply set $u_k(x) = 1$ for all k. However, if we are using the reduced-zone scheme, with $|k| \leq \pi/a$, this choice of $u_k(x)$ can be maintained only for the lowest band. When we go to the second band (or more precisely, what becomes the second band when a nonvanishing periodic potential is introduced), $u_k(x)$ must be chosen to be $e^{i2\pi x/a}$ for $-\pi/a \leqq k \leqq 0$, and $e^{-i2\pi x/a}$ for $0 \leqq k \leq \pi/a$, in order to reproduce the free-electron wavefunctions of the same energy. Note that both these have the required periodicity. For the higher bands, other periodic functions of the form $e^{\pm i2n\pi x/a}$ are required. Particular interest arises at the points of crossing of energy levels on the reduced-zone scheme, since that is where the periodic potential has the greatest effect. For example, at $k = \pi/a$, the wavefunctions for the first and second band are, respectively,

$$\psi_1 = 1 \cdot e^{i\pi x/a} \tag{8-13a}$$

and

$$\psi_2 = e^{-i2\pi x/a} \cdot e^{i\pi x/a} = e^{-i\pi x/a} \tag{8-13b}$$

Since these are degenerate, if there is any nonvanishing matrix element of $V(x)$ connecting them, the proper eigenfunctions are the sum and difference of ψ_1 and ψ_2, namely,

$$\psi_+ = \psi_1 + \psi_2 \sim \cos\frac{\pi x}{a} \tag{8-14a}$$

$$\psi_- = \psi_1 - \psi_2 \sim \sin\frac{\pi x}{a} \tag{8-14b}$$

We note in passing that both ψ_+ and ψ_- can still be written in the form (8-12) as our general theorem requires, but now $u_k(x) = (1 \pm e^{-i2\pi x/a})$.

We also note that ψ_+ and ψ_- differ only in phase, one being shifted by distance $a/2$ with respect to the other along the x axis. This is precis the shift required so that one will have the charge density centered at t center of the unit cell, while the other will have a node there, with the char piled up at the edge of the cell. Obviously, if there is any periodic potent

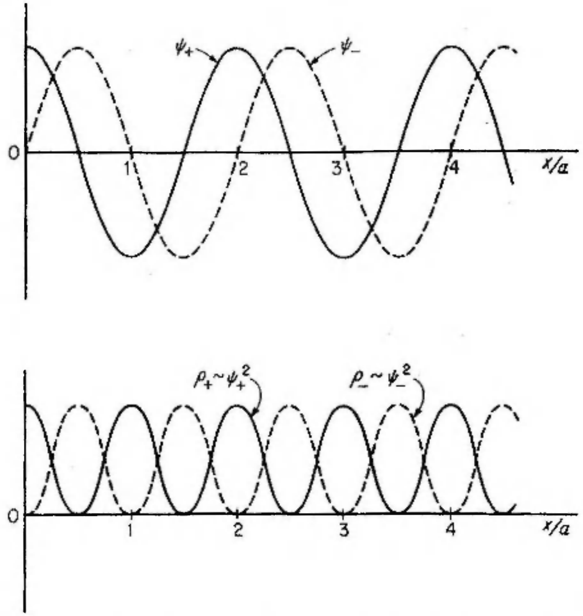


Fig. 8-3. *Band-edge wavefunctions at $k = \pi/a$ in the nearly free-electron approximation.*

at all, these two functions will have different energy, leading to the gap b tween the two bands indicated by the dotted curve in Fig. 8-2. The wid of the gap is just twice the matrix element connecting ψ_1 and ψ_2, as giv above. These wavefunctions are illustrated in Fig. 8-3.

If we now imagine that the periodic potential $V(x)$ is quite strong, th the free-electron wavefunctions are no longer suitable approximations to used in any reasonably rapidly convergent perturbation approximation. that case, one might consider the opposite limit, in which one considers electron as tightly bound to one atom along the chain, with the translation symmetry simply superimposed. That is, if $\varphi(x)$ is the wavefunction f the electron bound to one center, one can set up a periodic function $u_k(x)$ simply superimposing the $\varphi(x)$ from all the centers to form

$$u_k(x) \sim \sum_i \varphi(x - x_i) \qquad (8\text{-}1$$

When this $u_k(x)$ (which actually has no dependence on k in this approximation) is substituted into (8-12), we obtain the so-called "tight-binding approximation" to the wavefunction for energy-band electrons. From this point of view, the various bands result from various $\varphi(x)$. If we are considering actual energy bands in a three-dimensional solid, these will accordingly be characterized by the atomic state being used for $\varphi(x)$, so that one speaks of a $2s$ band or a $3d$ band, for example. This nomenclature has some meaning even when the binding is not very tight, and it is often used.

As the simplest example of the tight-binding approximation, let us consider the band in one dimension corresponding to the $1s$ band in a solid. In this case, $\varphi(x)$ is a nodeless function, decreasing smoothly from a maximum at the origin. Then the $u_k(x)$ constructed according to (8-15) will be a nodeless function with a maximum in each unit cell at the position of the nucleus, as illustrated in Fig. 8-4*a*. Now, at $k = 0$, $\psi_k(x) = u_k(x)$, and, instead of being a constant as in the free-electron case, the wavefunction has a peak in each unit cell. If we go to $k \neq 0$, then the e^{ikx} factor modulates the amplitude of the periodic function $u_k(x)$ as we move from one cell to the next in the crystal. This is illustrated in Fig. 8-4*b*, for the case of a k vector one-third of the way from the origin to the boundary of the first Brillouin zone. We plot only the real part of $\psi(x)$; the imaginary part has a modulating envelope displaced by $3a/2$. As a result the total charge-density distribution is the same in every cell. All that is modulated is really the phase of the wavefunction, just as in a free-electron traveling wave, $\psi \sim e^{ikx}$.

Moving on to the zone boundary, $k = \pi/a$, Fig. 8-4*c* and *d* shows the real and imaginary parts of $\psi(x)$. These two functions correspond to the ψ_+ and ψ_- of the free-electron case, illustrated in Fig. 8-3. As in that previous case, one of the functions peaks the charge density at the nuclei, whereas the other puts a node at the nucleus. In other words, Re $\psi(x)$ still has a $1s$-like character, whereas Im $\psi(x)$ has a $2p$-like character. Continuing on to $k = 2\pi/a$, Fig. 8-4*e* and *f* shows that the real and imaginary parts of $\psi(x)$ now look qualitatively like $2s$ and $2p$ functions, respectively, added in phase in each cell, corresponding to $k = 0$. Because, in fact $u_k(x)$ cannot be treated as independent of k in a rigorous way, these pictorial considerations must be viewed as highly approximate versions of the actual form of the wavefunctions. Nonetheless, they do show in a simple way that, even in the tight-binding approximation, there is some validity to the picture introduced earlier of the higher bands in the reduced-zone scheme arising from absorbing the extra nodes from the e^{ikx} function into the $u_k(x)$. Thus, Fig. 8-4*c* approximates the wavefunction from the lowest band at the zone boundary, whereas Fig. 8-4*d* approximates the second band there. Similarly, Fig. 8-4*e* approximates a $2s$-like band at the zone center, whereas Fig. 8-4*f* approximates a $2p$-like band there. We shall later go into more detail on the determination of these functions.

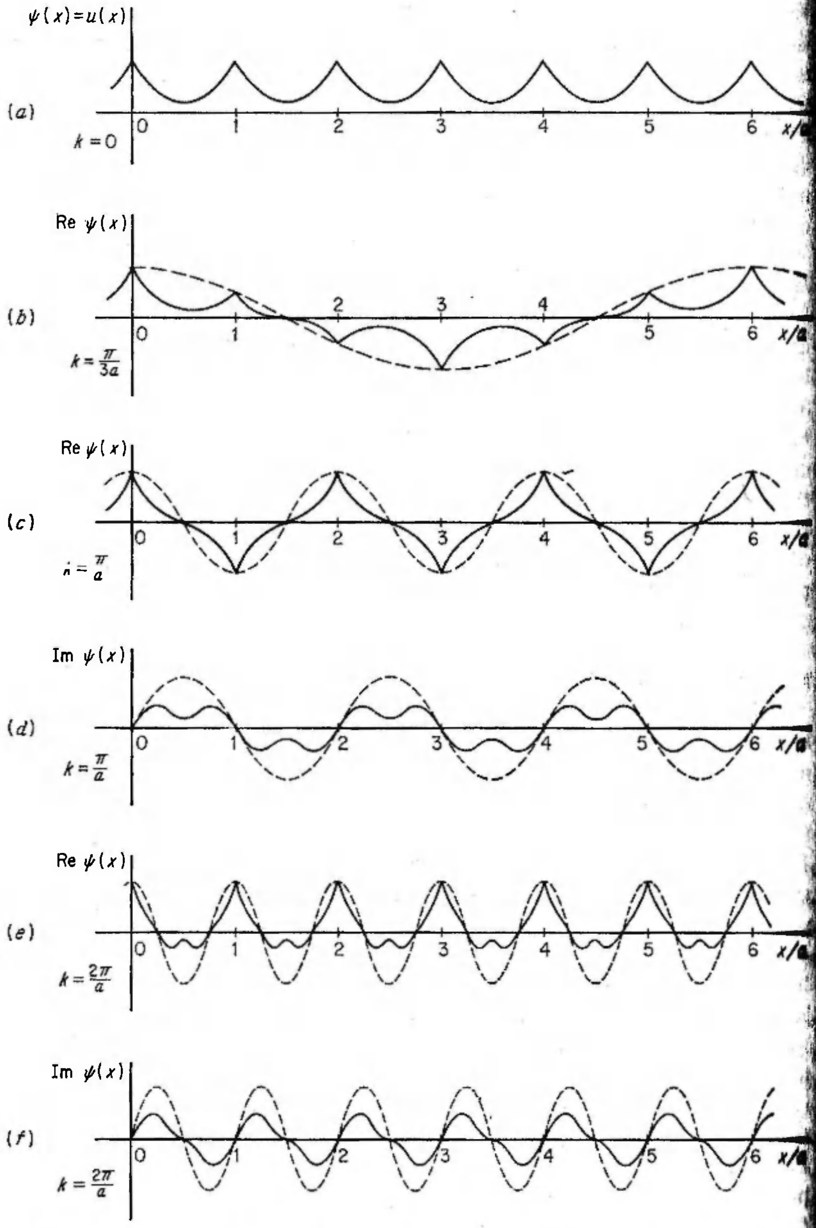


Fig. 8-4. *Representative tight-binding wavefunctions based on* 1*s function in each un cell.*

8-4 Crystal Symmetry and the Group of the *k* Vector

Let us consider the result of applying one of the transformation operators P_R, corresponding to one of the operations R of the point group, to a wavefunction in the Bloch form. That is, we consider

$$P_R\psi_{\mathbf{k}} = P_R u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \\ = u_{\mathbf{k}}(\mathbf{R}^{-1}\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{R}^{-1}\mathbf{r}} \tag{8-16}$$

If we note that applying the same orthogonal transformation to both vectors in a scalar product does not change the value of the product, we have

$$\mathbf{k}\cdot\mathbf{R}^{-1}\mathbf{r} = \mathbf{Rk}\cdot\mathbf{RR}^{-1}\mathbf{r} = \mathbf{Rk}\cdot\mathbf{r} \tag{8-17}$$

Inserting this result in (8-16) leads to

$$P_R\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{R}^{-1}\mathbf{r})e^{i\mathbf{Rk}\cdot\mathbf{r}} \tag{8-18}$$

Now, so long as we are dealing with a simple space group, all operations from the point group are also symmetry operations from the space group. Thus the function $u_{\mathbf{k}}(\mathbf{R}^{-1}\mathbf{r})$ is periodic if $u_{\mathbf{k}}(\mathbf{r})$ is, because $\mathbf{R}^{-1}\mathbf{a}_i$ must be a primitive translation if $\mathbf{a}_i$ is. Since periodicity is all that is required of $u_{\mathbf{k}}(\mathbf{r})$, we can rename $u_{\mathbf{k}}(\mathbf{R}^{-1}\mathbf{r}) = u'_{\mathbf{Rk}}(\mathbf{r})$ so as to conform to the general form. In that case, (8-18) becomes

$$P_R\psi_{\mathbf{k}}(\mathbf{r}) = u'_{\mathbf{Rk}}(\mathbf{r})e^{i\mathbf{Rk}\cdot\mathbf{r}} \tag{8-19}$$

where the prime on $u'_{\mathbf{Rk}}$ is to remind us that, if one chooses an $\mathbf{R}$ such that $\mathbf{Rk} = \mathbf{k}$, it need not be true that $u_{\mathbf{k}}(\mathbf{r})$ is also unaffected by the transformation. (In the usual case of no degeneracy, u' can differ from u only by a phase factor; if there is degeneracy, u' can be a linear combination of the degenerate functions u.) The conclusion from this argument, then, is that the effect of operating on $\psi_{\mathbf{k}}$ with P_R is to produce an eigenfunction also in Bloch form, but with the **k** vector simply rotated to **Rk**. This enables us to make a simple geometric inspection to find all the symmetry-related **k** vectors, all of which must have associated eigenfunctions of the same energy.

If one carries out successively all the point-group operations R on a given wave vector **k**, one generates what is known as the *star* of **k**. A number of typical cases are illustrated in Fig. 8-5, for the case of a two-dimensional square lattice. For example, if one takes a general **k**, located in no special symmetry direction, then each operation of the group will take it into a new position. In this case, the star will have h "points," one for each element of the group. If the **k** vector lies along a symmetry line as in Fig. 8-5*b* and *c*, then some of the symmetry operations will leave it unchanged and the star will have fewer points. If the **k** vector touches the zone boundary, there will in general be a reduction in the number of distinct **k** values in the star because any two which are related by a reciprocal-lattice vector $\mathbf{K}_m$ must be treated as identical and counted only once. This is illustrated for one pair in Fig. 8-5*d*. If the **k** vector lies on a symmetry plane and also on the zone boundary, further reductions in number occur. Finally, in Fig. 8-5f reach the point where all the symmetry-related **k** vectors are identical reciprocal-lattice vector displacements. In other words, the **k** vector m be considered invariant under all operations of the group, just as if it been $\mathbf{k} = 0$. Thus the symmetry at the corner of a square lattice is as as at the center.

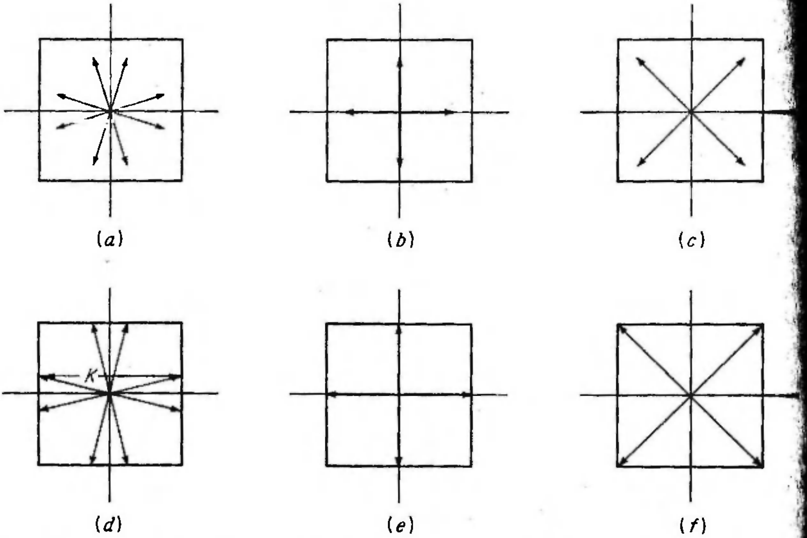


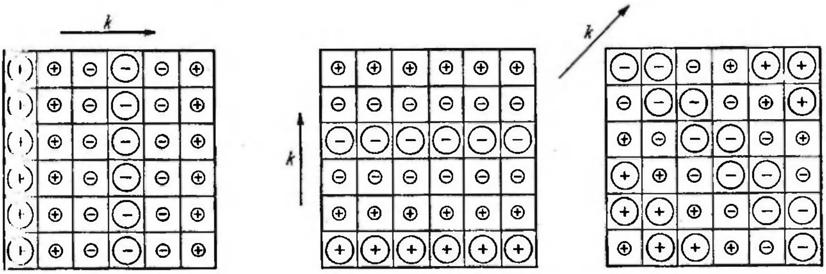
Fig. 8-5. *Typical examples of the star of the wave vector for the case of a tw dimensional square lattice. (a) General point, eight distinct k values; (b)-(c) symmet planes, four distinct k values; (d) general point on zone boundary, four distinct k valu after allowing for translational equivalence; (e)-(f) special points on zone boundary, tw and one distinct k values, respectively.*

It is clear that special interest is attached to symmetry points in **k**-spa which are left invariant by some of the group operations, since only the can symmetry-based degeneracy exist among functions with the same value. Those operators which leave a given **k** invariant form a subgrou of the entire point group, called the *group of the wave vector*. For exampl if **k** lies along the k_x axis, its group will include all rotations about the axis and all reflections in planes including the x axis. Now, under an oper tion of the group **k**, $\psi_{\mathbf{k}}$ may be left unchanged (apart from a phase facto perhaps), or else it may be transformed into a new function $\psi'_{\mathbf{k}}$, with the sa wave vector. In the latter case, there will be more than one distinct $u_{\mathbf{k}}($ associated with the same exponential factor $e^{i\mathbf{k}\cdot\mathbf{r}}$. These various $u_{\mathbf{k}}(\mathbf{r})$ wil transform among themselves under the group of **k** according to an irreducib representation of the group which is called the *small representation*.

To summarize, to specify completely the transformation properties of a wavefunction under the operations of the space group, it is necessary to give two bits of information. The first is the **k** vector, which specifies the transformation properties under translation and determines the star of **k**. The second is the small-representation label telling the symmetry properties of $u_{\mathbf{k}}(\mathbf{r})$ under the operations of the group of the wave vector. At a general point in **k** space, however, the group of the wave vector contains only the identity, and the small-representation label is not necessary.

8-5 Pictorial Consideration of Eigenfunctions

Before plunging into the full group-theoretical machinery required for a systematic study of the possible symmetries and degeneracies of energy bands



(a) (b) (c)

Fig. 8-6. *Schematic illustration of dependence of energy in an s band on the direction of the k vector.* (*a*) *and* (*b*) *have the same energy, being equivalent by symmetry.* (*c*) *need not have this same energy, even if* $|k|$ *is the same as in* (*a*) *and* (*b*), *because no symmetry operation connects the wavefunction of* (*c*) *with that of* (*a*) *or* (*b*). (*The real part of* ψ *is systematically shown in each case.*)

of all sorts, let us try to acquire a firm grasp of the qualitative symmetry considerations which our machinery will be handling. We can do this by inspecting simple sketches illustrating the form of the wavefunctions for successively more complicated situations. Perhaps the simplest case to consider is the case of an *s*-like band in the tight-binding approximation. In Fig. 8-4, we have already inspected the one-dimensional case. In going even to two dimensions, we can no longer plot the wavefunction in any simple way. Rather, we resort to a schematic diagram, in which the amplitude in each cell is indicated by the size of a pattern representing the symmetry of the cellular wavefunction. Thus in Fig. 8-6 we use a circle in each cell to represent an *s*-like wavefunction, the size of the circle representing the amplitude of the $e^{i\mathbf{k}\cdot\mathbf{r}}$ function, and the sign is indicated explicitly. In Fig. 8-6*a* and *b*, we show the appearance of the wavefunction for **k** vectors

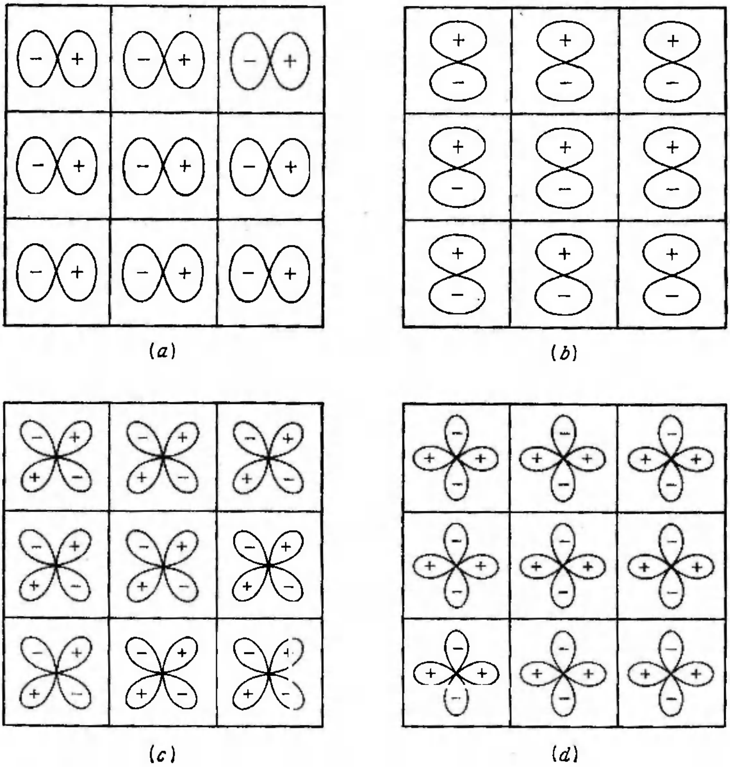
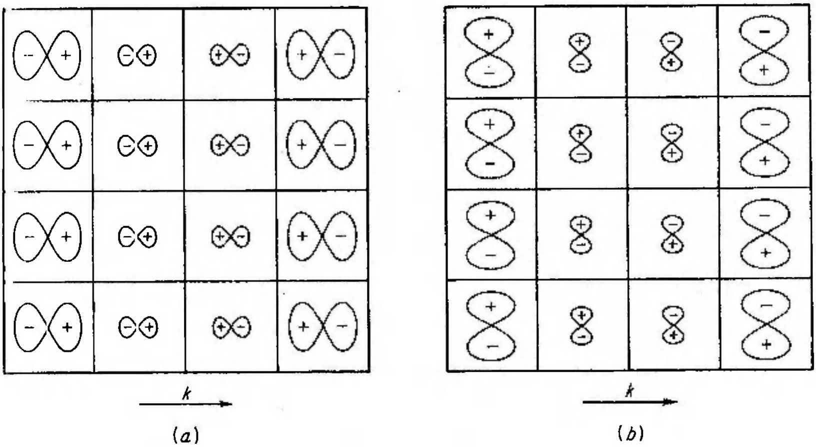


Fig. 8-7. *Symmetry aspects of p-like and d-like bands in cubic lattice at k = 0 (a)-(b) Two p-band wavefunctions related by a fourfold symmetry rotation, hen degenerate. (c)-(d) Representative d-band wavefunctions of symmetry T_{2g} and under the octahedral group O_h; these are not related by any symmetry operation, an hence they will not in general be degenerate.*

of equal magnitude, directed along k_x and k_y, respectively. Evidently th fourfold rotation relating x to y will transform one of the functions into th other, and they must be degenerate. When we consider Fig. 8-6*c*, however we see at a glance that there can be no symmetry operation which transform that wavefunction into either of the previous two. Thus, even if the mag nitude of the **k** vector is the same as in the first two cases, the energy nee not be the same, because the states are not related by symmetry. In othe words, the function $E(\mathbf{k})$ need not be spherical for electrons in bands; i need have only the symmetry of the point group of the crystal.

Another simple case to consider is that of $\mathbf{k} = 0$. Then the $e^{ik\cdot}$ factor in the wavefunction reduces to unity, and the wavefunction mu have exactly the same form in each cell. If we consider an s band, there is only one state with $\mathbf{k} = 0$ and no complications arise. However, if we go to a p band, there are three p functions to work with. If the point symmetry is as high as cubic, these are all related by symmetry operations of the group and they will be degenerate. This is illustrated by Fig. 8-7*a* and *b*. If the symmetry were lower, they would not be all degenerate (see Sec. 4-6). If we now proceed to a d band, then, even with a cubic point group, all five functions cannot be related by symmetry operations. Rather they separate into three degenerate functions of T_{2g} symmetry and two degenerate functions of E_g symmetry, as discussed in Chap. 4 in connection with the crystal-field splittings. These are illustrated in Fig. 8-7*c* and *d*. All these results are the same as if we had only one site to consider, because, for $\mathbf{k} = 0$, the translational symmetry from cell to cell does not lower the overall symmetry of the wavefunction by introducing a "special" direction.



(*a*) (*b*)

Fig. 8-8. *Schematic diagram showing how* $\mathbf{k} \neq 0$ *reduces the symmetry by eliminating the operation connecting* p_x *and* p_y *functions.*

The interesting novel cases arise when we combine the symmetry-lowering presence of a nonzero $\mathbf{k}$ vector with atomic symmetries of p and higher bands, where degeneracy may exist at $\mathbf{k} = 0$. The simplest example of this is the case of the three p-like functions, degenerate at $\mathbf{k} = 0$ in a cubic lattice, and transforming according to the irreducible representation T_{1u}. As soon as $\mathbf{k} \neq 0$, the three p-band (more precisely, T_{1u}) wavefunctions need not be connected by any symmetry operation. This is illustrated in Fig. 8-8, where the p_x and p_y bands are shown for the case of $\mathbf{k}$ lying along the k_x direction. Inspection immediately shows that these functions are no longer related by any symmetry operation of the point group. Hence they will in general have different energies. So long as **k** lies along k_x, however, the and p_z bands will remain degenerate. But if **k** takes on a general directio the point-group symmetry of the wavefunction is completely destroyed a no degeneracy will remain. These results are illustrated schematically Fig. 8-9. At each stage in this process of lowering the symmetry, the char terization of ψ by irreducible representation labels will of course be done

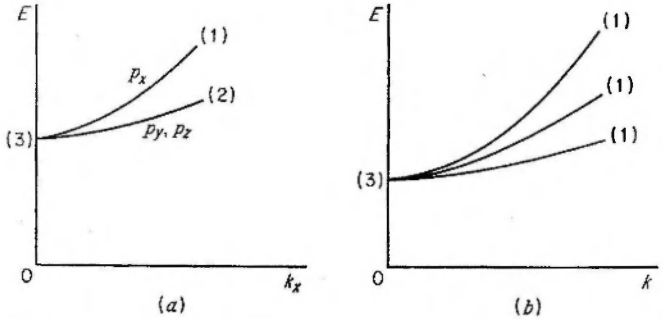


Fig. 8-9. *(a) Decrease of degeneracy in p band as k increases from zero along t k_x axis, leaving p_y and p_z bands still degenerate; (b) complete lifting of degeneracy whe k lies in a general direction.*

terms of the group of the wave vector for that particular **k**, because that i all the symmetry left in the problem after **k** has been specified.

8-6 Formal Consideration of Degeneracy and Compatibility

Having developed some feeling for the effect of the **k** vector on the symmetry of wavefunctions in crystals, let us now proceed to a more formal mathematical treatment. Our starting point is the Schrodinger equation for a single electron moving in the periodic crystalline potential $V(\mathbf{r})$, namely,

$$H\psi_{\mathbf{k}} = E\psi_{\mathbf{k}} \tag{8-20}$$

where

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) = -\left(\frac{\hbar^2}{2m}\right)\nabla^2 + V(\mathbf{r})$$

and where $\psi_{\mathbf{k}}$ must be in the Bloch form $u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$. If we substitute this form for $\psi_{\mathbf{k}}$ into (8-20), we are led, after canceling out the exponential factor common to each term, to

$$-\left(\frac{\hbar^2}{2m}\right)[\nabla^2 u + 2i\mathbf{k}\cdot\nabla u - k^2 u] + V(\mathbf{r})u = Eu$$

After a little rearranging, this can be written as

$$-\left(\frac{\hbar^2}{2m}\right)\nabla^2 u + [V(\mathbf{r}) + (\hbar/m)\mathbf{k}\cdot\mathbf{p}]u = E'u \tag{8-21}$$

where $E' = E - \hbar^2k^2/2m$ is the energy measured with respect to the kinetic energy of a free electron with the same $\mathbf{k}$ value. This equation (8-21) might be called a *pseudo-Schrodinger equation* for the periodic part $u(\mathbf{r})$ of the wavefunction. It contains the usual kinetic-energy part in $\nabla^2 u$, which would be the kinetic energy of the $u_\mathbf{k}(\mathbf{r})$ by itself. It also contains the periodic potential $V(\mathbf{r})$. However, the effective potential in the brackets contains another term, proportional to $\mathbf{k}\cdot\mathbf{p}$, which acts like a momentum-dependent potential. It is this new term which can be viewed explicitly as lowering the symmetry of the pseudo-Hamiltonian for determining energy levels for a prescribed $\mathbf{k}$ value.

The process of obtaining this pseudo-Hamiltonian may profitably be compared with the similar process followed in solving for the energy levels in the hydrogen atom. There we take advantage of the spherical symmetry to determine the angular form of the wavefunction in terms of spherical harmonics. This reduces the problem to the solution of a one-dimensional pseudo-Schrödinger equation for the radial function, in which the angular motion has been replaced by an effective centrifugal potential in the radial equation. In the present case, because we know from Bloch's theorem how the wavefunction must vary from cell to cell, we are able to reduce the problem to an equivalent one within one cell, but with a peculiar effective potential.

In analyzing the symmetry of the pseudo-Hamiltonian in (8-21), we know that the periodic potential $V(\mathbf{r})$ is invariant under all point-group operations. However, the $\mathbf{k}\cdot\mathbf{p}$ term in the effective potential is invariant only under the group of the wave vector at $\mathbf{k}$. This fact follows from the consideration (8-17) on recalling that $\mathbf{p}$ and $\mathbf{r}$ have the same transformation properties under all proper and improper rotations. Thus the appropriate symmetry group for the analysis of our eigenfunctions is that part of the point group which is also in the group of the wave vector. For example, in a simple cubic structure, the point group is O_h. At $\mathbf{k} = 0$, this is the appropriate group to use, since all point-group operations will leave $\mathbf{k} = 0$. If we then consider a nonzero $\mathbf{k}$ vector along the k_x axis, the symmetry is immediately reduced to the tetragonal group C_{4v}, which contains only the eight elements E, C_2, $2C_4$, $2\sigma_v$, $2\sigma_d$, all of which leave k_x unchanged. Since this group has four one-dimensional and one two-dimensional representation, the highest degeneracy is twofold. Thus the threefold degenerate, p-like T_{1u} states at $\mathbf{k} = 0$ must split for $k_x \neq 0$. Inspection of the character tables shows that T_{1u} must split into an A_1 and an E representation, when the symmetry is lowered from O_h to C_{4v}, in the manner described above. This relationship is described by saying that symmetries A_1 and E of the group C_{4v} for wav functions with **k** on the k_x axis are compatible with the symmetry T_{1u} o the group O_h for a wavefunction at $\mathbf{k} = 0$.

This concept of compatibility (introduced by Bouckaert, Smoluchowski and Wigner[1]) is the same as the one we considered earlier in conjunctio with the successive reduction of degeneracy by crystal fields of lower an lower symmetry; namely, if we consider a small term of the lower symmetry added as a perturbation to the Hamiltonian of higher symmetry, then th original eigenfunctions will still form zero-order eigenfunctions for the ne problem and also basis functions for representing the new smaller group A representation Γ_i of the subgroup is compatible with a representation Γ of the larger group if the basis for Γ_i is included in the basis for Γ_j. In terms of the representations themselves, the irreducible representation Γ_i

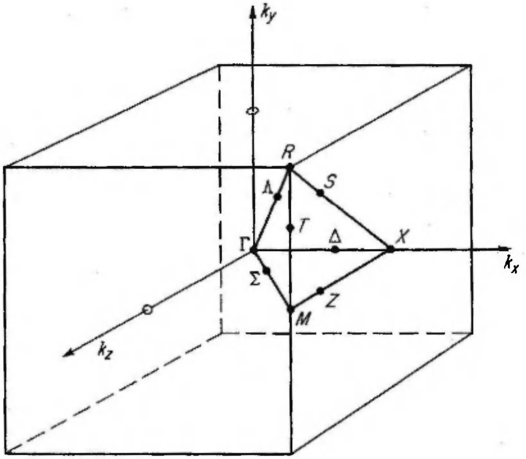


Fig. 8-10. *Simple cubic Brillouin zone with special points labeled.*

of the subgroup is compatible with the irreducible representation Γ_j of the full group if, and only if, Γ_i is present in the decomposition of Γ_j in terms of the irreducible representations of the subgroup. Whether or not this is true may be determined by analysis of only the characters of the representations, as we observed in considering the crystal-field problem.

To carry this discussion forward in concise and explicit terms, let us now introduce some examples of the conventional labeling of special symmetry points and lines in the Brillouin zone. The simplest example in three dimensions is the simple cubic case, shown in Fig. 8-10. In terms of the standard notation used in the figure, the case discussed above of a general point along the k_x axis corresponds to the point Δ, where the group of the **k** vector is C_{4v}. Let us systematically work out all the compatibility relations between symmetries at Γ ($\mathbf{k} = 0$) and Δ. In dealing with this problem in general it is customary to label the irreducible representations by indicating the special point under consideration, with a subscript indicating the particular irreducible representation for the appropriate group of the wave vector, the representations being simply numbered in a conventional order. Thus the information content of the representation labels commonly used in molecular work is given up in order to give the information on the **k** vector which is necessary for characterizing band wavefunctions. For an unambiguous labeling, it is necessary to specify the conventional order in terms of a character table. To illustrate, the character table at the point Δ may be written as shown in Table 8-1. We have also given the characters of the representations for the

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[1] L. P. Bouckaert, R. Smoluchowski, and E. P. Wigner, *Phys. Rev.*, **50,** 58 (1936).

Table 8-1

Character table at point Δ and characters of representations from Γ

C_{4v}	E	C_4^2	$2C_4$	$2\sigma_v$	$2\sigma_d$
Δ_1	1	1	1	1	1
Δ_2	1	1	−1	1	−1
Δ_3	1	1	−1	−1	1
Δ_4	1	1	1	−1	−1
Δ_5	2	−2	0	0	0
Γ_{1g}	1	1	1	1	1
Γ_{2g}	1	1	−1	1	−1
Γ_{3g}	2	2	0	2	0
Γ_{4g}	3	−1	1	−1	−1
Γ_{5g}	3	−1	−1	−1	1

full group O_h of the wave vector at the point Γ, labeled in the arbitrary number system of Bethe. In obtaining these characters from the tables for $O_h = O \times i$, we have quoted the even-parity cases and we have used the fact that σ_v is equivalent to iC_4^2, whereas σ_d is equivalent to iC_2. For the odd-parity cases, such as the p bands of $T_{1u} - \Gamma_{4u}$ symmetry discussed above, the characters for the reflections would be changed in sign because they are improper rotations. Given the information in this table, one can proceed by inspection of the characters (or by use of the decomposition formula) to find all the compatibility relations between Δ and Γ. These are given (for the even-parity cases) in Table 8-2. In the same manner, the compatibility relations between Σ and Γ can be worked out by using the subgroup C_{2v}, with the four one-dimensional representations Σ_1, Σ_2, Σ_3, and Σ_4. Finally, the compatibility between Λ and Γ can be worked out by using the subgroup C_{3v}, which has two one-dimensional representations Λ_1 and Λ_2

and a two-dimensional representation Λ_3. These results are also given the table.

To proceed with the discussion of compatibility, we now note that, one lets k increase along one of these symmetry directions toward t Brillouin-zone boundary, the symmetry increases suddenly when the boun ary is reached. The reason for this is illustrated in Fig. 8-5, which sho

Table 8-2

Compatibility relations between representations at Γ *and those at* Δ, Σ, *and* Λ

Γ_{1g}	Γ_{2g}	Γ_{3g}	Γ_{4g}	Γ_{5g}
Δ_1	Δ_2	Δ_1, Δ_2	Δ_4, Δ_5	Δ_3, Δ_5
Σ_1	Σ_3	Σ_1, Σ_3	$\Sigma_2, \Sigma_3, \Sigma_4$	$\Sigma_1, \Sigma_2, \Sigma_4$
Λ_1	Λ_2	Λ_3	Λ_2, Λ_3	Λ_1, Λ_3

that **k** vectors differing only by reciprocal-lattice vectors are to be consider identical. In our present example of the simple cubic lattice, when the poi Δ reaches the zone boundary at the point X, it suddenly becomes equivale to the **k** vector at $k_x = -\pi/a$. The group of the **k** vector then suddenly expanded by inclusion of a reflection plane perpendicular to the x directio and other associated symmetry elements, so that the group of the wave vect expands from C_{4v} to D_{4h}. This new group has 16 elements rather than and 10 rather than 5 classes. By the same methods used above, we can no set up a compatibility table relating the representations X_i of D_{4h} at X t the representations Δ_i of the subgroup C_{4v} at Δ.

The sudden increase in symmetry when the point Σ reaches the zone ed at M is even more dramatic, since all four corners of the section of the cu by the k_xk_z plane in Fig. 8-10 are related by reciprocal-lattice vectors. Th any operation taking M into itself or any of these other three equivale points is in the group of the wave vector. It is easy to see that the resultin symmetry group is D_{4h}. To find the compatibility relations between t representations M_i of D_{4h} at M and those of the subgroup C_{2v} at Σ, on again proceeds as above.

Finally, if the point Λ is allowed to move all the way out to the zon corner at R, one finds that the symmetry group suddenly expands from C to the full octahedral group O_h, because of the identity of all eight corne of the zone. This enables us to use Table 8-2 to specify the compatibili of the various representations R_i at R with those at Λ, since the Γ_i and t R_i will have the same characters and hence the same decompositions.

To complete the discussion of compatibility in this case, we now no that, since the symmetry (C_{4v}) at T is a subgroup of the symmetry groups both R and M, compatibility relations can be set up between the T_i and th

R_i and M_i. Similarly, relations can be set up between the S_i and the R_i and X_i and between the Z_i and the M_i and X_i. This completes the enumeration of the relations between symmetry points and lines. Evidently there are also entire planes of points having higher symmetry than points just off the plane, and similar arguments can be worked through to treat such cases. Given all these relations, one is finally in a position to determine whether or not a set of 10 symbols of the sort $\Gamma_i\ \Sigma_j\ \Delta_k\ \Lambda_l\ R_m\ T_n\ S_o\ Z_p\ M_q\ X_r$ does in fact specify a possible set of mutually compatible symmetries of the wavefunction at all symmetry points in the zone. If it does, then it describes the symmetry at all points in the zone of the eigenfunctions belonging to a possible single sheet of the $E(\mathbf{k})$ surface. Figure 8-11 illustrates schematically several sheets of this energy surface along two symmetry directions in **k** space, with compatible classifications according to Table 8-2.

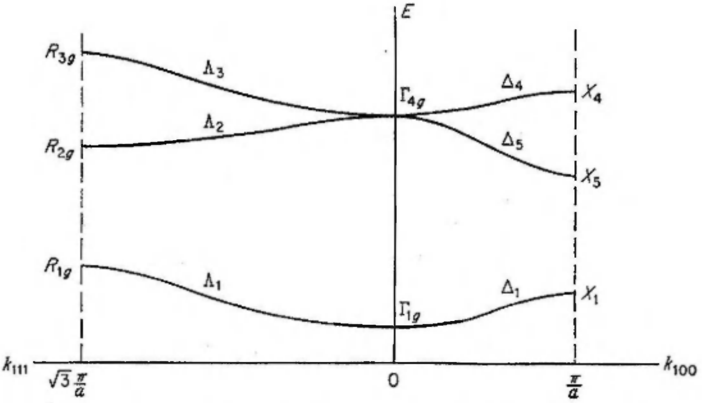

Fig. 8-11. *Schematic diagram of symmetry classifications along energy surfaces in two symmetry directions in k space.*

The example of the simple cubic lattice having been worked through in some detail, it should now be clear how other relatively simple cases can be handled. Diagrams showing the special symmetry points in the Brillouin zones of other structures and collections of character tables with various standard conventional labels for the irreducible representations are available in the literature.[1] For more details on more complicated cases, especially on nonsymmorphic space groups, the reader is also referred to the literature.[2]

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[1] See, for example, G. F. Koster, in F. Seitz and D. Turnbull (eds.), "Solid State Physics," vol. 5, p. 173, Academic Press Inc., New York, 1957.

[2] The classic paper underlying the present treatment is that of Bouckaert, Smoluchowski, and Wigner, *loc. cit.*; a more recent and pedagogical presentation is given by V. Heine, "Group Theory in Quantum Mechanics," Pergamon Press, New York, 1960.

8-7 Group Theory and the Plane-wave Approximation

Let us now turn from our study of the use of group theory to classify t symmetries of wavefunctions in various parts of the Brillouin zone and co sider a related application in which the symmetry is put to use in the simpl fication of the calculation of the actual wavefunctions and energies. W shall treat the plane-wave approximation, suitable, as discussed above, f the case of very loosely bound electrons. Actually, as pointed out b Herring,[1] the approximation may be made much more rapidly converge for the real cases of interest by orthogonalizing all the plane waves to th core electrons on each atom, since that automatically introduces the rap variations on each site which otherwise require a very large number of plan waves in an ordinary plane-wave expansion. This leads to what is call the *method of orthogonalized plane waves*, or for short, the OPW metho This method has been applied by numerous workers in actual calculatio of energy bands, and the underlying theory has also been put into ma different forms to bring out various aspects.[2] In particular, one can sho that there is a large degree of cancellation between the large negative-ener contribution from the strong attractive potential in the core region and th large kinetic energy produced by the rapid variation of ψ required by ortho onalization to the core wavefunctions. The small remaining differen can be treated as a weak "pseudopotential" perturbing simple plane wave Many aspects of the symmetry properties which we shall discuss here i conjunction with an ordinary plane-wave expansion can also be carri over directly into an OPW calculation; so the method is not without practic importance.

From Bloch's theorem, we know that we can always write the ban electron wavefunction in the form $\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$, where $u_{\mathbf{k}}(\mathbf{r})$ is period with the periodicity of the crystal lattice. Therefore, $u_{\mathbf{k}}(\mathbf{r})$ can be expand in a Fourier series (i.e., a series of plane waves $e^{i\mathbf{K}\cdot\mathbf{r}}$, with $\mathbf{K}$ being reciproc lattice vectors). That is, we write

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}'} U_{\mathbf{k}}(\mathbf{K}')e^{i\mathbf{K}'\cdot\mathbf{r}} \qquad (8\text{-}2$$

This form may now be substituted into (8-21), our pseudo-Schroding equation for the periodic part of the wavefunction. This leads to

$$\sum_{\mathbf{K}'} \left[\frac{\hbar^2 K'^2}{2m} + V(\mathbf{r}) + \frac{\hbar^2 \mathbf{k}\cdot\mathbf{K}'}{m}\right] U_{\mathbf{k}}(\mathbf{K}')e^{i\mathbf{K}'\cdot\mathbf{r}} = E'_{\mathbf{k}} \sum_{\mathbf{K}'} U_{\mathbf{k}}(\mathbf{K}')e^{i\mathbf{K}'\cdot\mathbf{r}} \qquad (8\text{-}2$$

If we multiply through by $e^{-i\mathbf{K}\cdot\mathbf{r}}$ and integrate, using the orthogonality o the plane waves, we obtain, after rearranging and reintroducing the to energy $E_{\mathbf{k}} = E'_{\mathbf{k}} + \hbar^2 k^2/2m$,

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[1] C. Herring, *Phys. Rev.*, **57**, 1169 (1940).

[2] See, for example, J. C. Phillips and L. Kleinman, *Phys. Rev.*, **116**, 287 (1959); a M. H. Cohen and V. Heine, *Phys. Rev.*, **122**, 1821 (1961).

$$\left[\frac{\hbar^2}{2m}(K^2 + 2\mathbf{K}\cdot\mathbf{k} + k^2) + V_{\mathbf{KK}} - E_{\mathbf{k}}\right] U_{\mathbf{k}}(\mathbf{K}) = -\sum_{\mathbf{K}'\neq\mathbf{K}} V_{\mathbf{KK}'} U_{\mathbf{k}}(\mathbf{K}') \tag{8-24}$$

In this,

$$V_{\mathbf{KK}'} = \Omega^{-1}\int V(\mathbf{r})e^{-i(\mathbf{K}-\mathbf{K}')\cdot\mathbf{r}}\, d\tau \tag{8-25}$$

where Ω is the normalization volume. Thus $V_{\mathbf{KK}'}$ is actually a function only of **K**-**K**′. In particular, $V_{\mathbf{KK}}$ is simply the average of the periodic potential over the unit cell, and it can be absorbed into the zero of the total energy $E_{\mathbf{k}}$. For simplicity, let us assume that this has been done in what follows. Given any periodic potential $V(\mathbf{r})$, the matrix elements $V_{\mathbf{KK}'}$ can be calculated from (8-25) in a straightforward manner. Given them, Eqs. (8-24) form a set of linear algebraic equations to be solved for the coefficients $U_{\mathbf{k}}(\mathbf{K})$ specifying the wave function $\psi_{\mathbf{k}}$ with energy $E_{\mathbf{k}}$. In general, one would need an infinite set of coefficients, and hence one would have to solve an impossibly large secular equation. However, a reasonable approximation can often be obtained by limiting the expansion to a relatively small number of plane waves. This is particularly true if an OPW expansion is actually being carried out. Thus it is worthwhile to consider the case of a finite set of plane waves to see how they may be most efficiently chosen and handled.

After absorbing the mean potential energy into the total energy, (8-24) can be written as

$$\left[E_{\mathbf{k}} - \frac{\hbar^2}{2m}(\mathbf{K}+\mathbf{k})^2\right] U_{\mathbf{k}}(\mathbf{K}) = \sum_{\mathbf{K}'\neq\mathbf{K}} V_{\mathbf{KK}'} U_{\mathbf{k}}(\mathbf{K}') \tag{8-26}$$

This form is familiar for the case of a perturbation calculation in which the diagonal energies are $\hbar^2(\mathbf{K}+\mathbf{k})^2/2m$ and the off-diagonal elements are the $V_{\mathbf{KK}'}$. As is well known, before perturbation theory can be applied, we must exactly diagonalize the Hamiltonian within any manifold of degenerate functions to get the proper zero-order linear combinations. Group theory is very helpful in carrying this out.

To illustrate this, consider the case of wavefunctions at $\mathbf{k} = 0$. Then the unperturbed energies are simply $\hbar^2\mathbf{K}^2/2m$, so that all plane waves with the same value of $|\mathbf{K}|$ will be degenerate. Barring accidental degeneracy, all such degenerate **K** values must be related by symmetry operations of the point group. For example, in the simple cubic case, the lowest nonzero **K** value is $(2\pi/a, 0, 0)$, which we abbreviate by introducing the Miller indices (100). Having the same energy as this plane wave will be the five others with indices (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$, and $(00\bar{1})$, where, for example, $(\bar{1}00)$ refers to $(-2\pi/a, 0, 0)$. Evidently, these are all interrelated by the operations of O_h. The next degenerate set, having twice the unperturbed energy, the set of 12 waves based on permutations of (110), allowing for nega values of the indices.

Now, since the six degenerate- (100) type waves comprise a complete of degenerate functions transforming into one another under the operatio of O_h, they must form the basis for a six-dimensional reducible representatio of that group. The character of this representation is readily found

Table 8-3

Characters of various plane-wave representations

O_h	E	$8C_3$	$6C_4$	$3C_4^2$	$6C_2$	i	$8iC_3$	$6iC_4$	$3iC_4^2$	$6iC$
(000)	1	1	1	1	1	1	1	1	1	1
(100)	6	0	2	2	0	0	0	0	4	2
(110)	12	0	0	0	2	0	0	0	4	2

considering the effect on this set of six **K** vectors of a typical operation from each class in the group, in a manner reminiscent of our analysis of the character of a set of σ bonds in Sec. 4-12. The characters for the first few sets of waves are given in Table 8-3. From these characters, in the usual manner, we find that

$$(000) \rightarrow A_{1g} = \Gamma_{1g} \tag{8-27a}$$

$$(100) \rightarrow A_{1g} + E_g + T_{1u} = \Gamma_{1g} + \Gamma_{2g} + \Gamma_{4u} \tag{8-27b}$$

$$(110) \rightarrow A_{1g} + E_g + T_{1u} + T_{2g} + T_{2u} = \Gamma_{1g} + \Gamma_{3g} + \Gamma_{4u} + \Gamma_{5g} + \Gamma_{5u} \tag{8-27c}$$

The particular linear combinations of the plane waves having these various symmetries can be found by using the basis-function generating machinery of Sec. 3-8 or in many cases simply by inspection. For example, if we consider the six (100) functions, it is evident that the completely symmetric combination schematically indicated by

$$\frac{[(100) + (\bar{1}00) + (010) + (0\bar{1}0) + (001) + (001)]}{\sqrt{6}}$$

belongs to Γ_{1g}. Similarly, for Γ_{4u}, by analogy with the three functions (p_x, p_y, p_z) we find

$$\frac{[(100) - (\bar{1}00)]}{\sqrt{2}}, \frac{[(010) - (0\bar{1}0)]}{\sqrt{2}}, \frac{[(001) - (00\bar{1})]}{\sqrt{2}}$$

whereas, for Γ_{3g}, we have

$$\frac{[(100) + (\bar{1}00) - (010) - (0\bar{1}0)]}{2},$$

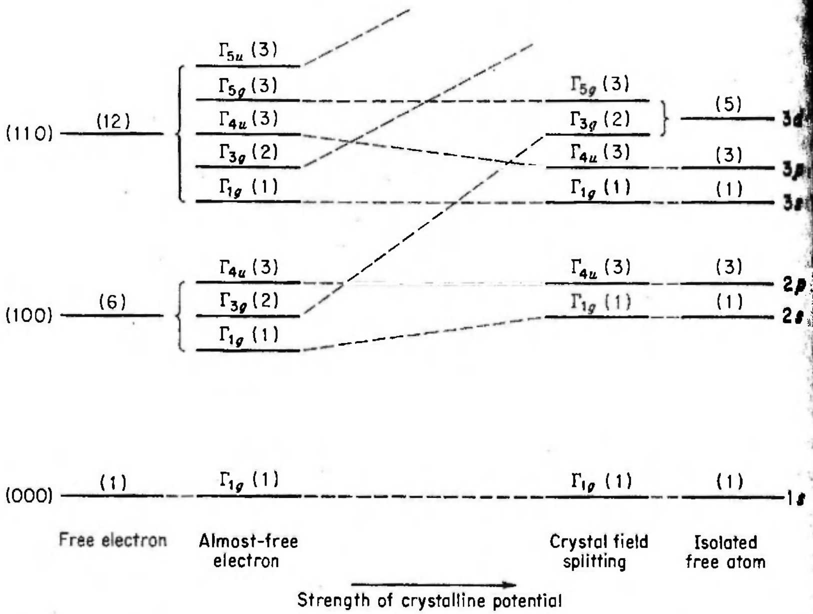
$$\frac{[(100) + (\bar{1}00) + (010) + (0\bar{1}0) - 2(001) - 2(001)]}{\sqrt{12}}$$

The linear combinations of definite symmetry having been found, our general matrix-element selection rule guarantees that the only matrix elements of the Hamiltonian will be between functions of the same symmetry. Thus, at $\mathbf{k} = 0$, even when we consider the 19 plane waves corresponding to (000), (100), and (110), we never have a secular equation larger than 3 × 3 to solve (for the Γ_{1g} case), and it is only a 2 × 2 for the Γ_{3g} and Γ_{4u} cases, and a 1 × 1 for the Γ_{5g} and Γ_{5u} symmetries. This accomplishes an enormous reduction in the algebraic effort, with no loss in accuracy.

If we leave the $\mathbf{k} = 0$ point, the lower resulting symmetry reduces the power of this method, because fewer plane waves will be degenerate. For example, in the simple cubic case at the point Δ, the group of the wave vector is only C_{4v}. In that case, of the (100) waves, only the four (010), $(0\bar{1}0)$, (001), and $(00\bar{1})$ are still degenerate. It is easy to show that these form a basis for a representation that decomposes into $\Delta_1 + \Delta_2 + \Delta_5$. The other two, (100) and $(\bar{1}00)$, each form bases for one-dimensional representations of symmetry Δ_1. Thus, even within only these six waves, there are three combinations of Δ_1 symmetry, and one no longer has such a large reduction in the size of the maximum secular equations. Obviously, if one went to a point of still lower symmetry, this method would be of still less help, and, at a completely general nonsymmetry point, it would be of no help at all. This emphasizes the fact that making an energy-band calculation of a given accuracy at a point of high symmetry is much easier than at a point of low symmetry because in the former case large numbers of plane waves are taken care of as a single unit by use of the symmetry of the situation. Although we have illustrated this fact only in the plane-wave approximation, it holds true in one form or another in all approximation methods.

8-8 Connection between Tight- and Loose-binding Approximations

Just as it was informative to set up a correlation diagram between the energy levels of molecules in the separated atom and united atom limits, it is also instructive to set up a correlation diagram relating the electronic energies in crystals in the tight- and loose-binding limits. To make such a diagram, one must choose some particular point in $\mathbf{k}$ space, while varying the strength of the crystal potential. For simplicity, we take $\mathbf{k} = 0$, since we have already treated both limits most carefully at that point. In the limit of no crystal potential, the energies are those of the (000), (100), (110), e plane waves, as discussed just above. In the opposite limit of extrem tight binding, the energies are just the usual atomic energy levels, as s by the crystalline field (of cubic symmetry for the case we are treatin Thus at either extreme the nature and energetic order of the levels are det mined by a relatively simple case. Since the group-theoretical symme



(110)
(12)
(100)
(6)
(000)
(1)
Γ_{5u} (3)
Γ_{5g} (3)
Γ_{4u} (3)
Γ_{3g} (2)
Γ_{1g} (1)
Γ_{4u} (3)
Γ_{3g} (2)
Γ_{1g} (1)
Γ_{1g} (1)
Γ_{5g} (3)
Γ_{3g} (2)
Γ_{4u} (3)
Γ_{1g} (1)
Γ_{4u} (3)
Γ_{1g} (1)
Γ_{1g} (1)
(5)
(3)
(1)
(3)
(1)
(1)
3d
3p
3s
2p
2s
1s
Free electron
Almost-free electron
Crystal field splitting
Isolated free atom
Strength of crystalline potential

Fig. 8-12. *Correlation diagram between loose-binding and tight-binding energy level at k — 0 in simple cubic case.*

classifications are rigorous, regardless of the strength of the potential, they can be followed through from one limit to the other. Noting that levels of the same symmetry cannot cross (because in general there will be an off-diagonal matrix element of the Hamiltonian, causing them to "repel" each other), we can rough in the entire diagram. The actual case would be expected to correspond to the level structure found at some intermediate potential strength in the diagram. Such a diagram is shown in Fig. 8-12 for the case at $\mathbf{k} = 0$. Note how strongly the relative positions of some levels shift with the tightness of binding. A similar diagram could be drawn for any other point in the zone, but the power of the symmetry classification would not be as great.

The experimental consequences of this level structure in determining the optical properties of solids, particularly in the ultraviolet region of the spectrum, have allowed quite detailed information to be obtained about the band structure in some cases. The reader is referred to the literature[1] for some specific examples.

8-9 Spin-orbit Coupling in Band Theory

So far, we have been considering the band theory of electrons moving in a periodic potential without taking any account of the electron spin. In this case the Hamiltonian operator is a simple real operator, and the Schrödinger equation reduces to a purely real differential equation whose eigenfunctions and eigenvalues are being sought. In the absence of spin-orbit coupling, these eigenfunctions can be combined with spin eigenfunctions to form solutions of the form

$$\psi_{\mathbf{k}+} = u_{\mathbf{k}}(\mathbf{r})e^{(i\mathbf{k}\cdot\mathbf{r})}\alpha \qquad \text{and} \qquad \psi_{\mathbf{k}-} = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}\beta \tag{8-28}$$

where α and β are the usual spin up and down eigenfunctions, with $S_z = \pm\frac{1}{2}$. This gives the usual twofold spin degeneracy associated with each of the spatial eigenfunctions which we have been treating.

In fact, there will be a spin-orbit coupling term in the Hamiltonian which will make the true situation more complicated than this. This subject was first treated in a thorough manner by Elliott,[2] and we give some of his results here. The form of the spin-orbit coupling term in the Hamiltonian may be found from Eq. (6-47) by the argument used to obtain (6-48), the usual form for the spin-orbit coupling in atoms, namely, $\xi(r)\mathbf{l}\cdot\mathbf{s}$. However, because there is no spherical symmetry in solids, the result must in general be left in terms of the gradient of the potential and the linear momentum operator. Thus one obtains

$$H_{\text{spin-orbit}} = \frac{\hbar}{2m^2c^2}(\nabla V \times \mathbf{p})\cdot\mathbf{s} \tag{8-29}$$

as the term to be added to the usual Hamiltonian. There are other relativistic terms, such as those in p^4 and in $\nabla V\cdot\mathbf{p}$, which arise if this result is obtained by systematic reduction of the Dirac equation from four-component to two-component form rather than by the simple argument of Chap. 6. These will be neglected, however, because they do not introduce any qualitatively new effects but simply produce quantitative shifts in the energy eigenvalues. Evidently, the term (8-29) must still have the full symmetry demanded by the space group, and so the Bloch form of the wavefunctions is maintained. However, because there is a spin-dependent operator the Hamiltonian, the eigenfunctions will no longer in general be eig functions of S_z. Thus, in general the eigenfunctions will be of the for

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[1] H. Ehrenreich and H. R. Phillip, *Phys. Rev.*, **128,** 1622 (1962); **129,** 1550 (1963).

[2] R. J. Elliott, *Phys. Rev.*, 96, 266, 280 (1954).

$$\psi_{\mathbf{k}} = [u_{\mathbf{k}+}(\mathbf{r})\alpha + u_{\mathbf{k}-}(\mathbf{r})\beta]e^{i\mathbf{k}\cdot\mathbf{r}} \qquad (8\text{-}3$$

For the case of nondegenerate bands (i.e., those with only the spin degenerac the admixture of the reversed spin direction in any given function will be o of the order of the ratio of an atomic spin-orbit energy ζ to the interban energy separation. At symmetry points, where there is orbital degenera however, there will in general be zero-order mixtures of both spin orientatio just as in the atomic case, and this will have important consequences in the d termination of symmetries and energy splittings. For example, when spi is included, we expect the Γ_{4u} functions, which transform like the three p functions, to split into a fourfold Γ_{8u} level corresponding to $j = \frac{3}{2}$ and a twofold Γ_{6u} level corresponding to $j = \frac{1}{2}$.

Considering the effect of including the spin more generally, we are confronted with a situation which is exactly analogous to that treated in Sec. 4-7, when the double groups were introduced to take care of the crystal-field splittings of states with half-integral angular momentum. For the simple space groups, which factor neatly into a group of pure point operations and a group of translations, the rules developed in Sec. 4-7 are adequate to handle the character tables of all the "extra" representations coming from the double-valued spinor functions. For the nonsimple space groups, complications arise in the enumeration of the group elements, but we shall not go into that here. Thus we can simply use the machinery of the double groups developed in Chap. 4 to work out the decomposition of the direct product of the representation Γ_i for the spatial part of the wavefunction with $D_{\frac{1}{2}}$ for the spin part. That is

$$\Gamma_i \times D_{\frac{1}{2}} = \sum_j a_{ij}\Gamma_j \qquad (8\text{-}31)$$

where $D_{\frac{1}{2}}$ stands for the representation obtained from the two spin functions under the group of the wave vector. For example, at $\mathbf{k} = 0$ in the simple cubic case, where the double group of the wave vector is O_h', $D_{\frac{1}{2}} = \Gamma_{6g}$. Taking the direct product of Γ_{6g} with the ordinary single-valued representations appropriate for the spatial functions, namely, $\Gamma_{1g,u}$ through $\Gamma_{5g,u}$, one finds the effect of adding spin upon the degeneracies of the energy bands at $\mathbf{k} = 0$. The results are

$$\begin{aligned} \Gamma_1 &\rightarrow \Gamma_6 \\ \Gamma_2 &\rightarrow \Gamma_7 \\ \Gamma_3 &\rightarrow \Gamma_8 \\ \Gamma_4 &\rightarrow \Gamma_6 + \Gamma_8 \\ \Gamma_5 &\rightarrow \Gamma_7 + \Gamma_8 \end{aligned}$$

with the parity being unchanged by the addition of the spin. Thus the only levels which are split by the inclusion of spin are the triply degenerate Γ_4 and Γ_5 levels.

8-10 Time Reversal in Band Theory

In Sec. 5-16 we discussed the nature of the time-reversal symmetry in quantum mechanics and in particular its implications concerning a possible increase in degeneracy because of the increased symmetry entailed. We noted that Wigner had shown that, although time reversal, being antiunitary, cannot be represented within our usual framework, the question of extra degeneracy can be resolved by a consideration of the representations of the usual unitary operators of the group and their complex conjugates. Specifically, he showed that there were three cases *a*, *b*, and *c*, listed in Table 5-4, which determine whether an extra doubling of the degeneracy due to time-reversal symmetry occurs. These considerations may be carried over directly into our considerations here, with the integral spin rules applying for the case of energy bands with neglect of spin and the half-integral spin rules applying for the case of energy bands with spin included.

To determine which of the cases *a* to *c* is applicable, the Frobenius-Schur test involving only characters, rather than the complete representations D, D^*, is more convenient. However, this test in its general form requires one to form the sum $\sum_R \chi(R^2)$ over all group elements to see whether it is equal to $\pm h$, or zero. Since a space group contains an infinite number of elements, h, this test as it stands is not practical. Fortunately, Herring[1] has simplified this test for space groups to a form involving only elements from the group of the wave vector. This simplified form is

$$\sum_{Q_0} \chi(Q_0{}^2) = \begin{cases} n & \text{Case } a \\ 0 & \text{Case } b \\ -n & \text{Case } c \end{cases} \tag{8-12}$$

where the elements Q_0 are those elements of the space group which take **k** into $-$**k** and n is the number of such elements. Evidently, $Q_0{}^2$ will then take **k** into itself, and hence $Q_0{}^2$ must be in the group of the wave vector at **k**. If the group of the wave vector G^k contains the inversion i, then the Q_0 are just the elements of G^k. If G^k does not contain i, then the Q_0 are the elements of iG^k. For example, in the simple cubic case treated earlier in this chapter, at the point Δ, the group of the wave vector is C_{4v}, which does not contain the inversion. Thus the elements Q_0 are those in iC_{4v}. When we form the elements $Q_0{}^2$ from these, the inversion drops out but for more general cases we must retain it. Using the characters given in Table 8-1 and the facts that $(C_4^2)^2 = E$ and $\sigma_v^2 = \sigma_d^2 = E$, we s that $\sum_{Q_0} \chi(Q_0^2) = 8 = n$ for all five ordinary representations. This corr sponds to case *a*, and since we are treating the spin-free case, Table 5 shows that there is no extra time-reversal degeneracy.

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[1] C. Herring, *Phys. Rev.*, **52**, 361 (1937).

If spin is included, each one-electron function has half-integral spin an the rules from the last column of Table 5-4 apply. If we consider $\mathbf{k}$ at general point in the zone, where there is no special symmetry, the group o the wave vector contains only the identity. In this case, the time-revers symmetry doubles the degeneracy, as required by Kramer's theorem, s that every level is doubly degenerate.

Returning for simplicity to the spin-free case, we note that time reversa always introduces inversion symmetry into the $E(\mathbf{k})$ function even if th inversion is lacking from the spatial symmetry of the lattice. This can b seen in an elementary way by noting that in the absence of spin the time-reversed function is found by taking the complex conjugate. Thus, if we start with a function $\psi_{\mathbf{k}} = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$, the time-reversed, and necessarily degenerate, function related to this is $\psi_{\mathbf{k}}^* = u_{\mathbf{k}}^*(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}$. But this latter function can be thought of as $\psi_{-\mathbf{k}} = v_{-\mathbf{k}}(\mathbf{r})e^{i(-\mathbf{k})\cdot\mathbf{r}}$. This $\psi_{-\mathbf{k}}$ has the same energy a $\psi_{\mathbf{k}}$, but transforms according to $-\mathbf{k}$. Thus the energy surfaces in $\mathbf{k}$ space have inversion symmetry regardless of whether the crystal has this symmetry in coordinate space. A further consequence may be deduced by considering a point at the center of a face of the Brillouin zone where $-\mathbf{k}$ is identical with $\mathbf{k}$ via a reciprocal-lattice translation. Thus $\psi_{-\mathbf{k}} = \psi_{\mathbf{k}}^* = \psi_{\mathbf{k}}$, and $\psi_{\mathbf{k}}$ is real, provided that the symmetry is low enough (as in a triclinic lattice) so that there is no degeneracy at this point. For the case of no degeneracy, one can draw the further conclusion that at such a point the gradient of $E(\mathbf{k})$ is zero. This can be seen analytically by noting that

$$E\left(\frac{\mathbf{K}}{2} - \delta\mathbf{k}\right) = E\left(\frac{-\mathbf{K}}{2} + \delta\mathbf{k}\right) = E\left(\frac{\mathbf{K}}{2} + \delta\mathbf{k}\right) \tag{8-33}$$

where we have successively used inversion symmetry and translational symmetry of the $E(\mathbf{k})$ function. Given (8-33), evidently grad $E(\mathbf{K}/2) = 0$ provided only that there is no degeneracy at $\mathbf{K}/2$ and that $E(\mathbf{k})$ has a continuous derivative at that point. This absence of a gradient of energy can also be anticipated by noting that for a real wavefunction, such as we have here at $\mathbf{K}/2$, the perturbation $(\hbar/m)(\mathbf{k}\text{-}\mathbf{K}/2)\cdot\mathbf{p}$ from (8-21), being purely imaginary, can have no first-order effect on the energy. Thus the energy change with $\mathbf{k}$ must start quadratically with components of $(\mathbf{k}\text{-}\mathbf{K}/2)$. In case of degeneracy, this conclusion need not hold, since (8-33) could be satisfied by two $E(\mathbf{k})$ curves crossing at $\mathbf{K}/2$ with finite equal and opposite slopes. Similarly, in the second view, in case of degeneracy, the proof of the reality of $\psi_{\mathbf{k}}$ fails, and hence the $(\mathbf{k}\text{-}\mathbf{K}/2)\cdot\mathbf{p}$ perturbation can have first-order effects.

8-11 Magnetic Crystal Groups

In the preceding section, we have treated the implications of time-reversal symmetry for the usual case of nonmagnetic crystals. We noted that the time-reversed state, of necessity degenerate, was in some cases distinct, leading to additional degeneracy if the reversed state was not related to the starting state by any other symmetry operation. Even if the reversed state was distinct, however, its charge density was always the same, because time reversal reverses currents but leaves charge density invariant. Thus, so far as energy or charge density is concerned, time reversal is always a symmetry operation. (It is of course understood that any "external" magnetic fields are reversed in the operation of time reversal by the reversal of the currents producing them.) Moreover, because of the equality of energy of the two states, they have equal statistical likelihood of occurrence. This leads to zero average current density in the usual case where thermally induced perturbations cause rapid fluctuation between the two degenerate states. The situation becomes quite different, however, when a (potentially) magnetic crystal is lowered through its Neel temperature T_N. At this temperature long-range magnetic order sets in through a cooperative action of the spins on the various sites, coupled together through the exchange interaction. Because this order extends over a macroscopic system, the fluctuations between time-reversed states can occur only by very unlikely processes. Hence, time-averaged net currents and magnetic moments will exist with a high degree of stability, or, more properly, metastability. The stability of these arrays makes it possible to determine the magnetic structure in such crystals by observing the scattering of neutrons by the magnetic forces arising from the magnetic atoms. Another manifestation of the magnetic ordering is that it introduces a spin-dependent potential in the Hartree-Fock equations, so that the effective one-electron potential is not invariant under time reversal. As a consequence, even Kramer's degeneracies will in general be lifted.

This magnetic ordering sets in as the temperature is *lowered* because the ordering lowers the entropy as well as the energy of the system, and hence the requirement of minimum free energy F ($= U\text{-}TS$) favors such a transition at low temperatures, where the entropy S is given less heavy negative weight in the free energy. In most cases the transition to the ordered state is of second order. That is, the averaged state of the system changes continuously at the transition point even though the symmetry is lowered discontinuously. This requirement of state continuity at the transition will enable us to draw some conclusions about the compatibility of symmetries in the magnetic and nonmagnetic states of a given crystal.

To provide a systematic basis for discussion of the symmetry properties of magnetic crystals, it is necessary to develop an extension of the ordinary theory of crystallographic space and point groups. These ordinary grou are appropriate for the characterization of the charge density $\rho(\mathbf{r})$ in crystal, such as is relevant in the analysis of X-ray diffraction data, f example. However, to characterize in addition the symmetries of dist butions of currents $\mathbf{j}(\mathbf{r})$ or magnetization $\mathbf{M}(\mathbf{r})$ requires a more general fra work. For example, the number of possible space groups increases fro 230 to 1,651,[1] and the number of point groups goes from 32 to 122. Th enlarged numbers of groups are often referred to as *Shubnikov*,[2] or *col* groups, because Shubnikov first worked out the theory of symmetry grou in which an operation interchanging black and white colors is considered addition to the usual geometric operations. This color change is of cour analogous to the reversal of spin or current directions under time revers although, being a scalar, it can represent only the reversal of a vector o fixed direction. Strictly speaking, since time reversal is an antiunitary o eration, the irreducible representations for the magnetic groups are n completely identical with those of the isomorphous groups treated b Shubnikov.

In these magnetic groups, there are two types of elements, those A not containing time reversal, and those $M_k = TA_k$, which do contain i The latter are sometimes referred to as *antioperators*, since they are an unitary (see Sec. 5-16). Since time reversal commutes with all spati operators and since T^2 is the identity (as a physical symmetry operator, wi no concern about phases of half-integral wavefunctions), we immediatel see that

$$A_i A_{i'} = A_{i''} \qquad A_i M_k = M_{k'} \qquad M_k A_i = M_{k''} \qquad M_k M_{k'} = A_i$$

Now, in building up the 122 magnetic point groups, we find three type of groups. The first type is the set of 32 ordinary point groups, with n antiunitary operators. Such a group would be the complete symmetry, fo example, in a ferromagnetic crystal with only the identity and the inversio as point operations. Evidently T would reverse the sense of spins an could not be a symmetry operation. The next type of point group is th set of 32 formed from the usual ones by adjoining the time-reversal operato so that, for all A_i in the group TA_i is also in the group. Since A_i include E, TA_i includes T itself. But T cannot be a symmetry operation in any magnetic crystal, since it reverses the sign of any magnetic moment. Thu this set of 32 groups would appear to be possible only for diamagnetic o paramagnetic crystals, which have no time-averaged magnetic moments. However, since the point-group operations are those obtained from the space group by setting all translations equal to zero, T is a possible point-group operation in an antiferromagnetic crystal if it always appears combined with a translation connecting two oppositely directed spins in identical chemical environments, as illustrated in Fig. 8-13*a*. Finally, there are the more interesting new cases, the 58 magnetic point groups which contain T only in combination with a spatial rotation or reflection. This restriction eliminates the case just mentioned in which a pure translation connects two states with spins reversed but all charge densities the same. The distinction is illustrated in one dimension in Fig. 8-13. If translation by a is denoted by A, then TA is a symmetry operation for the structure in Fig. 8-13*a*, but not for that in Fig. 8-13*b*. Thus (*a*) would have T in its point group, but (*b*) would not. Note that ferromagnetic or ferrimagnetic[1] crystals can never have T itself in the point group, even allowing for translations.

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[1] N. V. Belov, N. N. Neronova, and T. S. Smirnova, *Trudy Inst. Krist., Akad. Nauk S.S.S.R.*, **11**, 33 (1955); *Kristallografiya*, **2**, 315 (1957); English translation, *Soviet Phys.-Cryst.*, **2**, 311 (1957).

[2] A. V. Shubnikov, "Symmetry and Antisymmetry of Finite Figures," U.S.S.R. Press, Moscow, 1951.

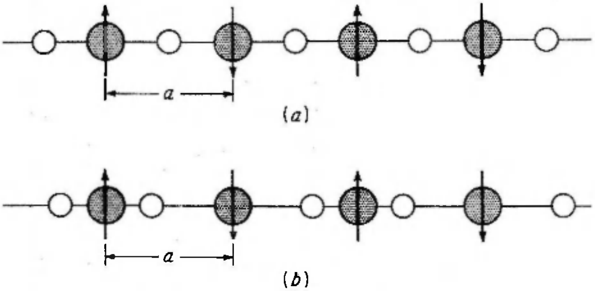

Fig. 8-13. *Two antiferromagnetic structures in one dimension.*

Let us now concentrate on the latter set of 58 point groups, since the first two sets of 32 can be handled simply by methods with which we have already dealt. We have noted that these 58 groups do not contain T itself. This can be generalized to the extent of excluding all elements of the form $M_k = TA_k$, where A_k is of odd order n, so that $A_k{}^n = E$. This is easily proved by noting that, if such an M_k is a group element, so is $M_k{}^n = (TA_k)^n = T^n(A_k)^n = T$, since n is odd, leading to a contradiction. Among the usual point-group elements, this excludes TC_3 as a possible element of these groups.

Now, designating one of these 58 groups by G, we note that it divides into two subsets of elements, the A_i and the $M_k = TA_k$, so that $G = \{A_i, M_k\}$. Following Tavger and Zaitsev,[2] we note further properties of G which allow us to construct all these groups, as follows:

1. The set of A_k and A_i are distinct; that is, no element A_j appears both with and without T. This is proved by noting that $A_j{}^{-1}$ must exist in G if A_j does, since G is a group. If TA_j were also to be in the grou then $TA_jA_j^{-1} = T$ would be also, since the group is closed. This wou be a contradiction of our requirement that T by itself not be in G.

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[1] A ferrimagnetic crystal has unequal antiparallel spins, leading to a net moment.

[2] B. A. Tavger and V. M. Zaitsev, *J. Exptl. Theoret. Phys.* (*U.S.S.R.*), **30**, 564 (1956); English translation, *Soviet Phys.* (*JETP*), **3**, 430 (1956).

2. If we replace T by E in the group $G = \{A_i, TA_k\}$, forming the set G' $\{A_i, A_k\}$, then G' is also a group and in fact is one of the usual 32 poi groups. Physically, this must be true, since when we replace T by E, w obtain covering operations of the charge density $\rho(\mathbf{r})$.

3. If we consider the group $G = \{A_i, M_k\}$, then the set $H = \{A_i\}$ form an invariant unitary subgroup of G which is one of the 32 ordinary poi groups. It is obvious that H forms a group, since the product of any tw A_i is again an A_i, and the identity and inverses must be included among th A_i since G was a group and since the product of an A_i with any M_k woul be an M_k. Since conjugation with any element involves multiplying by T or else not by T at all, either leading to an element of H, H is surely a invariant subgroup. Further, it is also an invariant subgroup of G', since setting $T \to E$ leaves this argument intact. The fact that it is a *point* group follows, since it is a subgroup of a point group.

4. Since H is an invariant subgroup of G (and G'), the number of elements in G (or G') must be an integral multiple of the number of elements in H (see Sec. 2-5). In fact, the number of elements in G must be twice the number in H; in other words, the number of unitary operators A_i must equal the number of antiunitary ones $M_k = TA_k$. This is readily seen, since if we multiply each A_i by some M_k, we produce as many distinct M_k as there are A_i. Hence the number of M_k must be at least as large as the number of A_i. Conversely, if we multiply each M_k by some $M_{k'}$, we produce as many distinct A_i as there are M_k. To reconcile these results, the number of A_i and M_k must be equal. Thus $\{M_k\} = \{TA_k\}$ is the only coset of H in G, and $\{A_k\}$ is the only coset of H in G'. One can further show that, if H is an invariant subgroup of index 2 with respect to *any* point group G', then $G = H + T(G' - H)$ must form a group, which will be one of the type we are considering. In this, $G' - H = C$ is the coset of H with respect to G'. The proof follows immediately upon recalling that the multiplication table of the factor group (see Sec. 2-8) involving only H and C requires that $H \cdot H = H$, $H \cdot C = C \cdot H = C$, and $C \cdot C = H$. Thus

$$G \cdot G = (H + TC) \cdot (H + TC) = (H + TC) = G$$

and G forms a group.

Given the above results, we can set up a simple procedure for finding all the magnetic groups. Start with one of the ordinary point groups G'. Find all its invariant subgroups of index 2, called H_r. Then, for each H_r, set up the magnetic group $G = H_r + T(G' - H_r)$. In the Schoenflies notation, this magnetic group is denoted by $G'(H_r)$, which gives a complete specification. By successively considering all 32 of the G', one finds all 58 of the magnetic point groups G. These are listed in Table 8-4, where we list all H for each G'. (For convenience, we also list the 32 groups not containing T, so that all elements are unitary and $H = G'$.) To facilitate reference to the literature, we also give the corresponding labels in the Shubnikov and the international notations. As explained more fully in Appendix B, in the international notation a number n represents an n-fold axis, n represents an n-fold rotation combined with inversion, and the letter m represents a mirror plane. In the magnetic groups, the underscore on an element means that it is to be combined with T. Thus the international notation combines the symbol for G' with underscoring, which gives information equivalent to the specification of the subgroup H. The Shubnikov notation is rather similar to the international notation, except that n refers to S_n rather than iC_n and the single dot refers to parallel elements and the double dot to perpendicular ones. As we shall not be using them, we shall not give further details on these notations here.

To illustrate the general considerations discussed above, let us consider the group C_{2h}, which has the four elements E, C_2, σ_h, i. Since the square of each of these elements is E, we see that there are three ways to choose the invariant subgroup, namely, (E, i), (E, C_2), and (E, σ_h). These correspond to the three successive entries under $G' = C_{2h}$ in Table 8-4 (excepting the group with no antielements). In each case, the other two elements of the group form the coset which is to be multiplied by T. For example, in the magnetic group $C_{2h}(C_2)$, the elements are E, C_2, $T\sigma_h$, Ti. The other magnetic groups $C_{2h}(C_i)$ and $C_{2h}(C_{1h})$ are formed in a similar manner.

8-12 Symmetries of Magnetic Structures

As an illustration of the use of these magnetic groups to characterize structures, consider the hypothetical orthorhombic ferromagnetic unit cell shown in Fig. 8-14. In the disordered state above T_N there would be no averaged magnetic moments on the sites, and the point group would be D_{2h}. When the order sets in as shown, the symmetry changes. The unitary group of symmetry operations decreases to C_{2h}, and the magnetic symmetry group is then $D_{2h}(C_{2h})$. To verify these statements, we note that D_{2h} contains the elements E, C_{2x}, C_{2y}, C_{2z}, σ_x, σ_y, σ_z, and i. (We associate x with the a axis, etc.) Evidently, these are all symmetry operations for the nonmagnetic state. In the magnetic state, however, C_{2x} and C_{2y}, for example, lead to a configuration in which all spins are reversed. Thus they can be in the magnetic group only in conjunction with T. C_{2z} remains in the group, since it leaves the spins unchanged. Recalling that spins or magnetic moments are axial vectors, we see that σ_z leaves the spins unchanged, whereas σ_x and σ_y reverse them. Also, inversion leaves the spin directions unchanged,

Table 8-4

Magnetic point groups

As indicated in the text, each mixed magnetic group can be characterized by giving a po group G' and an invariant unitary subgroup H of index 2. All 58 such groups are listed h together with the alternative Shubnikov and international notations. In the latter notatio one takes the symbol for G' and underscores those elements to which T has been adjoined. W also list the 32 point groups not containing T at all, in which the unitary subgroup is the entl group G'; hence, in these cases H is of index 1. We do not list the other 32 point groups, whi are obtained by adjoining T to all elements of G' to make a group of double size. The fir column indicates whether the structure is ferromagnetic (F) or antiferromagnetic (AF). Th 32 doubled point groups, which we have omitted, may be either diamagnetic or paramagnet or else antiferromagnetic if T is always coupled with a translation.

Crystal system	*Group G′*	*Number of elements*	*Invariant unitary subgroup H*	*Shubnikov notation*	*International notation*	*Magnetic order*
Triclinic	C_1	1	C_1	1	1	F
	$S_2(C_i)$	2	S_2	$\bar{2}$	$\bar{1}$	F
			C_1	$\underline{\bar{2}}$	$\underline{\bar{1}}$	AF
Monoclinic	C_{1h}	2	C_{1h}	m	m	F
			C_1	$\underline{m}$	$\underline{m}$	F
	C_2	2	C_2	2	2	F
			C_1	$\underline{2}$	$\underline{2}$	F
	C_{2h}	4	C_{2h}	$2{:}m$	$2/m$	F
			C_i	$\underline{2}{:}\underline{m}$	$\underline{2}/\underline{m}$	F
			C_2	$2{:}\underline{m}$	$2/\underline{m}$	AF
			C_{1h}	$\underline{2}{:}m$	$\underline{2}/m$	AF
Rhombic	C_{2v}	4	C_{2v}	$2\cdot m$	$2mm$	AF
			C_{1h}	$2\cdot m$	$2\underline{m}m$	F
			C_2	$2\cdot\underline{m}$	$2\underline{mm}$	F
	D_2	4	D_2	$2{:}2$	222	AF
			C_2	$2{:}\underline{2}$	$2\underline{22}$	F
	D_{2h}	8	D_{2h}	$m\cdot 2{:}m$	mmm	AF
			C_{2h}	$\underline{m}\cdot 2{:}m$	$\underline{mm}m$	F
			C_{2v}	$m\cdot 2{:}\underline{m}$	$mm\underline{m}$	AF
			D_2	$\underline{m}\cdot 2{:}\underline{m}$	$\underline{mmm}$	AF
Tetragonal	C_4	4	C_4	4	4	F
			C_2	$\underline{4}$	$\underline{4}$	AF
	S_4	4	S_4	$\bar{4}$	4	F
			C_2	$\underline{4}$	$\underline{\bar{4}}$	AF
	C_{4h}	8	C_{4h}	$4{:}m$	$4/m$	F
			C_{2h}	$\underline{4}{:}m$	$\underline{4}/m$	AF
			C_4	$4{:}\underline{m}$	$4/\underline{m}$	AF
			S_4	$\underline{4}\cdot\underline{m}$	$\underline{4}/\underline{m}$	AF
	D_{2d}	8	D_{2d}	$\bar{4}\cdot m$	$42m$	AF
			C_{2v}	$\underline{4}\cdot m$	$\bar{4}\underline{2}m$	AF
			D_2	$\underline{\bar{4}}\cdot m$	$\bar{4}2\underline{m}$	AF
			S_4	$\bar{4}\cdot\underline{m}$	$\bar{4}\underline{2m}$	F
	C_{4v}	8	C_{4v}	$4\cdot m$	$4mm$	AF
			C_{2v}	$\underline{4}\cdot m$	$4\underline{m}m$	AF
			C_4	$4\cdot\underline{m}$	$4\underline{mm}$	F
	D_4	8	D_4	$4{:}2$	42(422)	AF
			D_2	$\underline{4}{:}2$	$\underline{4}2$	AF
			C_4	$4{:}\underline{2}$	$4\underline{2}$	F
	D_{4h}	16	D_{4h}	$m\cdot 4{:}m$	$4/mmm$	AF
			D_{2h}	$m\cdot\underline{4}{:}m$	$\underline{4}/mmm$	AF
			C_{4h}	$m\cdot 4{:}m$	$4/\underline{mmm}$	F
			D_{2d}	$m\cdot\underline{4}{:}\underline{m}$	$\underline{4}/\underline{m}mm$	AF
			C_{4v}	$m\cdot 4{:}\underline{m}$	$4/\underline{m}mm$	AF
			D_4	$\underline{m}\cdot 4{:}m$	$4/\underline{mmm}$	AF

Table 8-4—continued

Crystal system	*Group G′*	*Number of elements*	*Invariant unitary subgroup H*	*Shubnikov notation*	*International notation*	*Magnetic order*
Rhombohedral	C_3	3	C_3	3	3	F
	S_6	6	S_6	$\bar{6}$	3	F
			C_3	$\underline{\bar{6}}$	$\underline{\bar{3}}$	AF
	C_{3v}	6	C_{3v}	$3\cdot m$	$3m$	AF
			C_3	$3\ \underline{m}$	$3\underline{m}$	F
	D_3	6	D_3	$3:2$	32	AF
			C_3	$3:\underline{2}$	$3\underline{2}$	F
	D_{3d}	12	D_{3d}	$\bar{6}\ m$	$3m$	AF
			S_6	$\bar{6}\cdot\underline{m}$	$\bar{3}\underline{m}$	F
			C_{3v}	$\underline{\bar{6}}\cdot m$	$\underline{\bar{3}}m$	AF
			D_3	$\underline{\bar{6}}\cdot\underline{m}$	$\underline{3m}$	AF
Hexagonal	C_{3h}	6	C_{3h}	$3:m$	$\bar{6}$	F
			C_3	$3:\underline{m}$	$\bar{6}$	AF
	C_6	6	C_6	6	6	F
			C_3	$\underline{6}$	6	AF
	C_{6h}	12	C_{6h}	$6:m$	$6/m$	F
			S_6	$6:\underline{m}$	$6/\underline{m}$	AF
			C_{3h}	$\underline{6}:m$	$\underline{6}/m$	AF
			C_6	$6:m$	$6/m$	AF
	D_{3h}	12	D_{3h}	$m\ 3:m$	$\bar{6}m2$	AF
			C_{3v}	$m\cdot 3:\underline{m}$	$\bar{6}m\underline{2}$	AF
			D_3	$m\ 3:\underline{m}$	$\underline{\bar{6}m}2$	AF
			C_{3h}	$m\cdot 3:m$	$6\underline{m2}$	F
	C_{6v}	12	C_{6h}	$6\cdot m$	$6mm$	AF
			C_{3v}	$6\cdot m$	$6m\underline{m}$	AF
			C_6	$6\cdot\underline{m}$	$6mm$	F
	D_6	12	D_6	$6:2$	$62(622)$	AF
			D_3	$6:2$	62	AF
			C_6	$6:\underline{2}$	$6\underline{2}$	F
	D_{6h}	24	D_{6h}	$m\cdot 6:m$	$6/mmm$	AF
			D_{3d}	$m\cdot 6:\underline{m}$	$6/m\underline{mm}$	AF
			C_{6h}	$m\cdot 6:m$	$6/m\underline{mm}$	F
			D_{3h}	$m\cdot 6:m$	$6/m\underline{m}m$	AF
			C_{6v}	$m\cdot 6:\underline{m}$	$6/\underline{m}mm$	AF
			D_6	$\underline{m}\cdot 6:\underline{m}$	$6/\underline{mmm}$	AF
Cubic	T	12	T	$3/2$	23	AF
	T_h	24	T_h	$\bar{6}/2$	$m3$	AF
			T	$\bar{6}/2$	$m3$	AF
	T_d	24	T_d	$3/\bar{4}$	$43m$	AF
			T	$3/\bar{4}$	$\bar{4}3m$	AF
	O	24	O	$3/4$	$43(432)$	AF
			T	$3/\underline{4}$	$\underline{4}3$	AF
	O_h	48	O_h	$\bar{6}/4$	$m3m$	AF
			T_h	$\bar{6}/4$	$m3\underline{m}$	AF
			T_d	$\bar{6}/4$	$m3m$	AF
			O	$\underline{\bar{6}}/4$	$\underline{m}3\underline{m}$	AF

because they are axial vectors. From this enumeration, we see that the magnetic symmetry group contains the elements E, C_{2z}, σ_z, i, TC_{2x}, TC_{2y}, $T\sigma_x$, and $T\sigma_y$, as required for $D_{2h}(C_{2h})$.

As a more realistic example introducing further features, consider the tetragonal antiferromagnetic unit cell shown in Fig. 8-15. This is the

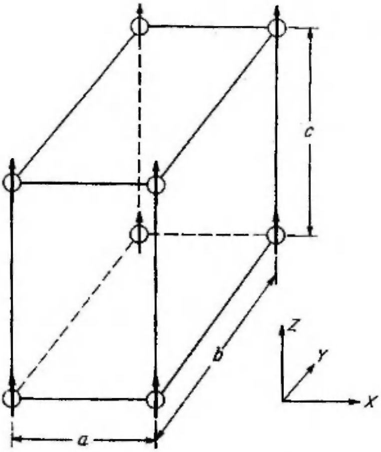

Fig. 8-14. *Orthorhombic ferroma*
unit cell of $D_{2h}(C_{2h})$ symmetry.

structure of the antiferromagnets MnF_2, FeF_2, and CoF_2, for exam which have the rutile structure. The shaded circles represent the me ions and the hollow circles the fluorine ions. The translations $\mathbf{a}_1$ and in the xy plane are of equal length a, and the third orthogonal translat $\mathbf{a}_3$ is of length c in the z direction. Although this diagram shows eight spins and only one down spin, the structure is antiferromagnetic since each the eight corner ions is "shared" among eight such cells which touch same corner. We note that the magnetic lattice has the same primi

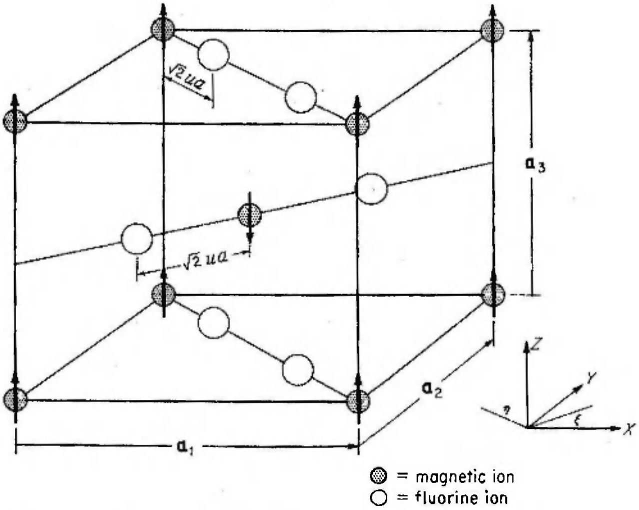
$\sqrt{2}ua$
$\mathbf{a}_3$
$\sqrt{2}ua$
$\mathbf{a}_2$
$\mathbf{a}_1$
Z
Y
X
η
ξ
● = magnetic ion
○ = fluorine ion

Fig. 8-15. *Tetragonal antiferromagnetic unit cell.* ($|\mathbf{a}_1| = |\mathbf{a}_2| = a$; $|\mathbf{a}_3| = c \neq$

translations as the paramagnetic one, because the different orientation of the fluorine neighbors distinguishes the body-center magnetic ions from the corner ions even in the disordered state. Thus there are two metal ions in the chemical as well as the magnetic unit cell. This would not be the case if the fluorine ions were not present. The presence of two metallic ions per unit cell introduces some symmetry operations involving the nonprimitive translation $\boldsymbol{\tau}_0 = \frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$ connecting the two metallic ions. In the paramagnetic state we have 16 symmetry operations involving either no translation or the nonprimitive translation $\boldsymbol{\tau}_0$. In our space-group-element notation $\{R \mid \mathbf{t}\}$, where R represents a rotation or reflection and $\mathbf{t}$ a translation, these are:

1. $\{E \mid 0\}$
2. $\{C_2 \mid 0\}$
3. $\{C_{2\xi} \mid 0\}$
4. $\{C_{2\eta} \mid 0\}$
5. $\{C_4 \mid \boldsymbol{\tau}_0\}$
6. $\{C_4^{-1} \mid \boldsymbol{\tau}_0\}$
7. $\{C_{2x} \mid \boldsymbol{\tau}_0\}$
8. $\{C_{2y} \mid \boldsymbol{\tau}_0\}$
9. $\{i \mid 0\}$
10. $\{\sigma_h \mid 0\} = \{C_2 \mid 0\}\{i \mid 0\}$
11. $\{\sigma_{d\xi} \mid 0\} = \{C_{2\xi} \mid 0\}\{i \mid 0\}$
12. $\{\sigma_{d\eta} \mid 0\} = \{C_{2\eta} \mid 0\}\{i \mid 0\}$
13. $\{S_4^{-1} \mid \boldsymbol{\tau}_0\} = \{C_4 \mid \boldsymbol{\tau}_0\}\{i \mid 0\}$
14. $\{S_4 \mid \boldsymbol{\tau}_0\} = \{C_4^{-1} \mid \boldsymbol{\tau}_0\}\{i \mid 0\}$
15. $\{\sigma_{vx} \mid \boldsymbol{\tau}_0\} = \{C_{2x} \mid \boldsymbol{\tau}_0\}\{i \mid 0\}$
16. $\{\sigma_{vy} \mid \boldsymbol{\tau}_0\} = \{C_{2y} \mid \boldsymbol{\tau}_0\}\{i \mid 0\}$

The rotations C_4 and C_2 are about the z axis, whereas $C_{2\xi}$ and $C_{2\eta}$ are rotations about axes parallel to $(\mathbf{a}_1 \pm \mathbf{a}_2)$. We note that the second eight of these are simply the products of the first eight with the inversion $\{i \mid 0\}$. All space-group operations for this crystal are built up from these 16 operations combined with translations by multiples of the primitive displacements. Now, the rule for finding the point group from this space group is to set all translations, primitive and nonprimitive, equal to zero, since these translations do not affect the macroscopic crystal symmetry under point operations. Thus the point group is just $D_4 \times i = D_{4h}$, even though the operations of the form $\{R \mid 0\}$ actually present in the space group would form only $D_2 \times i = D_{2h}$. This is an example of a nonsimple space group, in which the entire point group is *not* a subgroup of the space group.

Continuing to the ordered state of MnF_2, for example, we have the spin arrangement shown in Fig. 8-15. Considering in turn the 16 operations listed above, we find that the unitary subgroup of symmetry operations contains the following eight elements: $\{E \mid 0\}$, $\{C_2 \mid 0\}$, $\{C_{2x} \mid \boldsymbol{\tau}_0\}$, $\{C_{2y} \mid \boldsymbol{\tau}_0\}$, and the products of these with the inversion. Thus the unitary subgroup is $D_2 \times i = D_{2h}$, and, in the Schoenflies notation, the magnetic group would be $D_{4h}(D_{2h})$. One might note that the spins must lie along the z axis in crystal to be consistent with this point group. For example, if the were to be tipped to lie on the x direction, the magnetic symmetry g would be reduced to $D_{2h}(C_{2h})$, with the C_2 axis being the x axis. Su reduction in symmetry is obvious, since if the spins point along x, it longer equivalent to y and so the point group cannot be tetragonal. Be of magnetostriction, the symmetry of $\rho(\mathbf{r})$ will also be lowered by a tip of the spins, as is indicated by the change of G' from D_{4h} to D_{2h}.

It is also instructive to consider the symmetry situation which w prevail if the fluorine ions were not present in the structure. In that in the paramagnetic state, the unit cell would be only half as large, taining only one magnetic atom, since the translation $\boldsymbol{\tau}_0$ (by itself) w be a symmetry operation of the translation group. In the language crystallography, the Bravais lattice would be body-centered tetragonal rat than the primitive tetragonal Bravais lattice characteristic of the magn structure or of the chemical structure with fluorine atoms present. A result of the doubling of unit-cell size in going from the disordered to ordered state, the Brillouin-zone size would be cut in half. This natur has characteristic effects on the band structure of the crystal. Anot thing to notice is that, although the magnetic point group of the actual M crystal is $D_{4h}(D_{2h})$, it would be the group $D_{4h} \times T$ (one of the 32 omitted fr Table 8-4) if the fluorines were not there. Thus the nonmagnetic ions c not be ignored in determining questions of symmetry.

Enumeration of ferromagnetic groups. Having gained some familia with the significance of these groups, we can now readily work out which the groups require an antiferromagnetic structure and which can have a ferromagnetic moment. We have already noted that the 32 groups of form $G' \times T$ can be either diamagnetic or paramagnetic, or else antifer magnetic with T coming in only through antitranslations. For the other groups listed in Table 8-4, the structures cannot be diamagnetic or par magnetic, because then T by itself would be a symmetry operation, a none of these 90 groups has this operation included. Many of them cann be ferromagnetic (F) because some operation of the group will reverse the si of an antiaxial vector (such as the magnetization) for all possible orientation These then must be antiferromagnetic (AF). The results are given in the la column of Table 8-4. To see how these may be obtained, we note that t magnetization vector must in general lie along any two-, three-, four-, or six-fo axes that might be present, and perpendicular to any mirror planes. Howev it must also be perpendicular to any twofold antiaxis and parallel to any ant mirror plane. With these rules, it is easy to verify the entries in the tabl and to work out the direction in which the magnetization must point in eac ferromagnetic case. There are 31 groups consistent with a ferromagnet moment in some direction. The others must be antiferromagnetic for al spin orientations. For further details and a discussion of the symmetry restrictions on piezomagnetism, Hall effect, etc., see the review of Le Corre.[1]

One caution should be exercised in using these results: the spatial structure referred to here is that in the magnetic state, which may differ from that in the paramagnetic state. For example, a cubic material cannot be ferromagnetic according to our table. What this means is that, if a moment exists in a crystal which was cubic in the paramagnetic state, it must distort slightly on ordering (the process of magnetostriction) so as to reach a symmetry group compatible with a ferromagnetic moment. For example, if **M** lies on a fourfold axis, the group must be one of the tetragonal magnetic groups compatible with $\mathbf{M} \neq 0$ which is an invariant subgroup of the initial group. The index of the subgroup will then give the number of distinct directions in which the magnetization might lie in different domains of the crystal. Thus, if the original group was $O_h \times T$ and the final group is $D_{4h}(C_{4h})$, the number of domain directions would be $(48 \times 2)/16 = 6$. These six directions correspond to the positive and negative x, y, and z directions, which are the directions compatible with the fourfold symmetry.

8-13 The Landau Theory of Second-order Phase Transitions

The above considerations can be put on a more precise basis if one restricts attention to the immediate vicinity of the phase transition between the paramagnetic and the ordered state of the crystal. As stated earlier, this transition will normally be of second order, so that the state of the system on the ordered side of the transition ($T < T_N$) will approach arbitrarily close to the disordered state as $T \rightarrow T_N$. Thus, there is a discontinuity of symmetry at T_N, with no discontinuity of state. We can characterize the change in symmetry most easily by giving the symmetry group G_0 in the paramagnetic state and that G_1 in the ordered state immediately below T_N. One can then apply a general theory due to Landau[2] for treating the symmetry change in such a second-order transition.

We start by defining a generalized density function $\rho(\mathbf{r})$ which expresses the spatial distribution of charge and magnetic moment. In the higher symmetry state with space group G_0, this density will be taken to be $\rho_0(\mathbf{r})$, which must of course be invariant under all the transformations in G_0. Since G_0 contains T, ρ_0 must have no magnetic-moment density. Below T_N, we assume that $\rho(\mathbf{r})$ can be written as $\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r})$. Because any function can be decomposed into parts transforming according to the rows of the irreducible representations of any group (Sec. 3-8), we can in particular use the representations of G_0 to write

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[1] Y. Le Corre, *J. phys. radium*, **19**, 750 (1958).

[2] See, for example, L. D. Landau and E. M. Lifshitz, "Statistical Physics," chap. 14, Pergamon Press, Addison-Wesley Publishing Company, Inc., Reading, Mass., 1958.

$$\rho(\mathbf{r}) = \sum_{j,\kappa} c_\kappa^{(j)}\varphi_\kappa^{(j)} \qquad (8\text{-}3$$

Since ρ_0 is invariant under G_0, it is represented by only a single term in expansion, namely, the one from the one-dimensional identical representatio As any contribution to $\delta\rho$ having this symmetry cannot give a magne moment, it will not be important in the expansion of $\delta\rho$. Thus the e pansion (8-34) actually refers to $\delta\rho$, apart from the term invariant under

Next we consider the free energy Φ of the crystal. This will be a functio of the external parameters pressure and temperature and of the intern state parameters $c_\kappa^{(j)}$ specifying the state of the system. As the pressu and temperature are varied, the $c_\kappa^{(j)}$ shift to minimize Φ, as is required maintain the equilibrium state of the system, and of course the $\varphi_\kappa^{(j)}$ will al change, though maintaining their symmetry. Denote the free energy at th transition point by Φ_0. At this point, all $c_\kappa^{(j)} = 0$, except that from th identical representation. Since the change of state is continuous in a second order phase transition, we know that the other $c_\kappa^{(j)}$ start with vanishing small values at the transition and increase as T drops below T_N. Thi suggests that we should be able to expand Φ as a power series in the c_κ near the transition point. The form of this series is controlled by the fa that the free energy must be invariant under all symmetry transformation of G_0 because it must be valid through the transition point. Now the c_κ must transform under symmetry operations in the same way as the $\varphi_\kappa^{(j)}$ the product ρ is to have a unique value independent of the choice of co ordinate system. Thus the same combinations of the $c_\kappa^{(j)}$ as of the φ_κ form invariants. The transformation properties of products are found from direct products of the irreducible representations. Recalling ou matrix-element selection rules, an invariant can be obtained only from th product of a representation with itself. (Throughout this discussion, pair of complex-conjugate representations are treated as single irreducible representations.) Moreover, by the generalized Unsold theorem (Sec. 4-9 the sum of squares of the partners in an irreducible representation form such an invariant. Thus we take the expansion of Φ near the transition to begin with the terms

$$\Phi = \Phi_0 + \sum_j{}' A^{(j)}(P,T) \sum_\kappa [c_\kappa^{(j)}]^2 \qquad (8\text{-}35)$$

where the prime on the sum denotes the absence of the term from the identical representation.

Since the crystal must be invariant under G_0 at T_N, the values $c_\kappa^{(j)}$ must be all zero there in equilibrium. From a consideration of first and second derivatives, this requires that all the $A^{(j)}$ be nonnegative. If they were all positive, however, all the $c_\kappa^{(j)}$ would remain zero through the transition region and no transition would occur. Thus one of the $A^{(j)}(P, T)$ must vanish at

T_N, as it changes from positive to negative. Denote it by $A^{(j')} = a(T - T_N)$. Then, for $T > T_N$, all the $c_\kappa^{(j)}$ are zero; for $T < T_N$, the $c_\kappa^{(j')}$ for this particular representation j' become nonzero, and we can write

$$\delta\rho = \sum_\kappa c_\kappa^{(j')} \varphi_\kappa^{(j')} \tag{8-36}$$

Thus we have the general result that the magnetic order set up in a second-order phase transition from the paramagnetic state transforms like the basis functions of a single irreducible representation of the space group G_0 of the paramagnetic crystal. The symmetry operators leaving $\rho_0 + \delta\rho$ invariant evidently form a subgroup G_1 of G_0. The determination of the particular linear combination of $\varphi_\kappa^{(j')}$ within a representation is more intricate, since it depends on the higher-order invariants which keep $\delta\rho$ from increasing without bound for $T < T_N$. We shall not go into this here. Upon cooling a finite distance below T_N, one can no longer expect that $\delta\rho$ will consist of basis functions from a single irreducible representation, as in (8-36). Rather, one expects odd "harmonics" from higher-order terms in the expansion to come in. However, the symmetry group G_1 defined by the invariance of (8-36) should remain valid until another transition occurs at still lower temperatures.

These points are illustrated by an example, treated by Dimmock,[1] in which the magnetic-moment density just below T_N has the form

$$\rho \sim \mu_x (T_N - T)^{\frac{1}{2}} \cos \frac{2\pi x}{3a}$$

corresponding to a single irreducible representation of the space group having $k = 2\pi/3a$. This introduces a magnetic superlattice with period $3a$ rather than the chemical-cell period a. At lower temperatures, Dimmock shows that one might expect ρ to include a third harmonic term $\sim\mu_x(T_N - T)^{\frac{3}{2}} \cos (2\pi x/a)$, representing a "sharpening" of the structure. Still higher terms would in general also be expected, but, for a structure with magnetic ions only at $x = 0, a/2, a, 3a/2, \ldots$, the two terms above represent the most general spatial variation obtainable from higher odd powers of the initial density. The higher terms would affect the temperature dependences, however. We note that although the term in $\cos (2\pi x/a)$ no longer belongs to the same irreducible representation of the paramagnetic space group G_0, as does $\cos (2\pi x/3a)$, it does have the same symmetry group G_1, because any operation leaving $\cos (2\pi x/3a)$ invariant also leaves $\cos (2\pi x/a)$ invariant. This is consistent with our general conclusions stated above.

8-14 Irreducible Representations of Magnetic Groups

For many applications, it is necessary to know the irreducible representations of the groups, not just the structures of the groups themselves. For example, the wavefunctions of localized states in a crystal are characterized by i reducible representations of the point group of the symmetry about t local site (which may be considerably smaller than the macroscopic poi group of the crystal structure). On the other hand, for discussion of no localized states extending over the periodic structure of the crystal, use o the full space-group representations is essential. The nonlocalized states t be dealt with are of two major sorts: the electronic energy-band states, considered earlier in the chapter for nonmagnetic crystals, and spin wave state The latter are a type of excitation of the magnetic system in which there a small deviations from alignment by spins on all sites rather than a fu quantum unit of spin deviation on a single site. The phases of the deviation at the various sites are related by the same exponential factor $e^{i\mathbf{k}\cdot\mathbf{r}}$ whic Bloch's theorem required for the electronic excitations. Within the un cell, however, the symmetry of the spin wave excitation is that of the lowerin operator S_- referred to a quantization axis along the ordered spin directio of the atom concerned, rather than the symmetry of an atomic electroni wavefunction as in the electronic energy bands.

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[1] J. O. Dimmock, *Phys. Rev.*, **130**, 1337 (1963).

The methods for handling the representations of the magnetic group have been discussed in some detail by Dimmock and Wheeler[1]. We shal not go into the complications of the full discussion. However, we not several points. The presence of the antiunitary operators associated wit time reversal precludes the possibility of ordinary matrix representations, as we noted in Sec. 5-16. Rather, one must settle for corepresentations, which require the insertion of complex-conjugate signs into certain of the product relations. Still, it is possible to reduce questions of degeneracy to a discussion involving only the unitary subgroup of the full magnetic group, in an extension of the work of Herring referred to in Sec. 8-10. In this way, the discussion of compatibility relations between symmetries of the electronic wavefunctions at various symmetry points and lines in the Brillouin zone can be extended to the case of magnetic crystals, in which time reversal is not a symmetry operator. In addition to the compatibility relations among the various parts of the zone, one can also work out compatibilities between the symmetries in the paramagnetic state and in the ordered state below T_N, which will describe how degeneracies are lifted by the reduction of symmetry on going from G_0 to G_1. One difficulty which arises is that if the magnetic unit cell is larger than the chemical one, owing to a magnetic-superlattice structure, then the magnetic Brillouin zone will be smaller than the chemical one. In this case, some **k** values which have special symmetry properties because they are on the surface of the magnetic zone will lack these symmetries in the chemical zone. Thus, in these cases, the magnetic symmetry group G_1 is not, in fact, a subgroup of the nonmagnetic group G_0. Although these cases require special handling, the discussion of Dimmock and Wheeler shows that no serious difficulty results.

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[1] J. O. Dimmock and R. G. Wheeler, *J. Phys. Chem. Solids*, **23**, 729 (1962); *Phys. Rev.*, **127**, 391 (1962).

EXERCISES

8-1 For nearly free electrons, it is often useful to use the extended-zone scheme, with the approximation that the wavefunctions are nearly $e^{i\mathbf{k}\cdot\mathbf{r}}$ and the energies are nearly $E(\mathbf{k}) = \hbar^2k^2/2m$, with $\mathbf{k}$ being allowed to range far beyond the first Brillouin zone, as described in Sec. 8-2. By graphical construction, find the first four zones for the square lattice, the first two being indicated in Fig. 8-1. For the higher zones, show how the pieces fit together within the first zone. Using the free-electron approximation for the energy, sketch energy contours in the reduced-zone scheme for all four of these zones.

8-2 Any one-dimensional periodic potential can be Fourier analyzed into a series $V(x) = \sum_{n=-\infty}^{\infty} V_n\, e^{2\pi inx/a}$. $(V_{-n} = V_n^*$, since V is real.) Use this potential in a perturbation treatment of the energy levels and wavefunctions of a nearly free electron. Note that special handling of two nearly degenerate functions is required whenever k is nearly equal to an integral multiple of π/a. Show that the two eigenvalues at such k values differ by just twice the matrix element connecting the two zero-order plane-wave states. Show that there is a quadratic variation of energy with k near such points, and relate the coefficient to the gap between the two energies, showing that a small gap produces a rapid variation with k, corresponding to a small *effective mass*. On the other hand, show that, for the lowest state at $k = 0$, the effective mass is always greater than the true mass.

8-3 Generalize Exercise 8-2 to the case of three dimensions with arbitrary reciprocal lattice.

8-4 (*a*) Apply the results of Exercise 8-2 to the case in which the potential consists only of the $|n| = 1$ terms in the expansion, and take V_1 real so that the potential is even about the origin. (*b*) Apply the results of Exercise 8-2 to the case of a *square-wave potential*, in which $V(x)$ is an even function such that $V(x) = -v$ for $|x| < a/4$ and $V(x) = +v$ for $a/4 < |x| < 3a/4$, with a periodicity of a. The results of these perturbation approaches will be valid only for weak potentials. Exact solutions to these problems can be obtained, the first in terms of Mathieu functions[1] and the second by piecing together solutions for constant potentials.[2]

8-5 Consider a two-dimensional square lattice, with symmetry group C_{4v}. The Brillouin zone will also be square, and the various symmetry points and lines are as indicated in Fig. 8-16. Find the group of the wave vector at each of the points Γ, Σ, Δ, X, M, and Z. For each of these groups write down character tables to establish an unambiguous notation. Then work out *all* the compatibility relations between adjacent points, and write out several sets of mutually compatible symmetries for all points.

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[1] J. C. Slater, *Phys. Rev.*, **87**, 807 (1952).

[2] R. de L. Kronig and W. G. Penney, *Proc. Roy. Soc. (London)*, **A130**, 499 (1931).

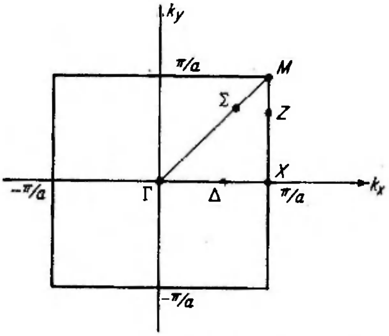

Fig. 8-16. *Special points in square Brillouin zone.*

8-6 Consider a tetragonal lattice whose point group is D_{4h}. The reciproc lattice is also tetragonal, and the cross section of the first Brillouin zone at th horizontal reflection plane is a square. Within this plane, special points can b labeled as in Fig. 8-16. (*a*) What is the group of the wave vector at each of th labeled symmetry points? (*b*) Work out the compatibility relations between th irreducible representations at Γ, Σ, and M.

8-7 Continue the analysis of the plane-wave expansion at $\mathbf{k} = 0$ given i Sec. 8-7, carrying it through the (111), (200), (210), and (211) waves, as well a those treated in the text. Find all the symmetries which can be obtained from ea set of degenerate waves. Work out explicit linear combinations for all th symmetries obtainable from the (110)-type waves.

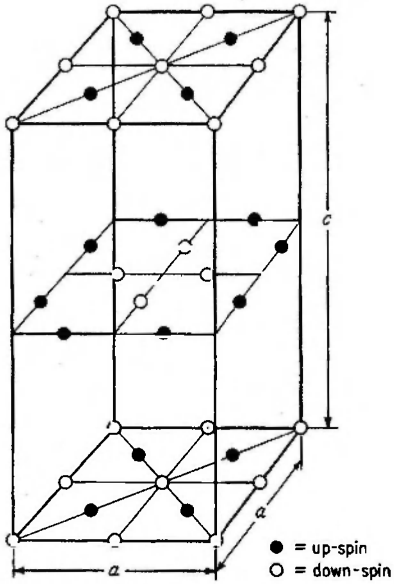

Fig. 8-17. *Tetragonal magnetic structure.*

8-8 Consider the tetragonal magnetic structure shown in Fig. 8-17, where the spin directions up and down are parallel to the fourfold axis. (*a*) What are the point groups of this structure in the paramagnetic state and in the ordered state shown in the figure? (*b*) Does symmetry allow a ferromagnetic moment? Explain in some detail why the apparent cancellation of moments in the figure is not rigorously required by symmetry. This is an example of what is called *feeble*, or *parasitic*, ferromagnetism.[1]

8-9 In the paramagnetic state, the crystals of MnO, FeO, CoO, NiO, MnS, and MnSe have the face-centered cubic NaCl structure shown in Fig. 8-18. (Point group is $O_h \times T$.) In the antiferromagnetic state, all the magnetic ions in a given (111) plane have their spins parallel. The spin directions of these planes alternate from one (111) plane of magnetic ions to the next. The magnetic symmetry group depends on the axis of orientation of the spins. Consider the following orientations: (*a*) the [111] direction perpendicular to the planes of parallel spins; (*b*) an [001] direction; (*c*) an $[01\bar{1}]$ direction lying in the (111) plane; (*d*) a general direction having no special symmetry. For each of these orientations, find the magnetic point group, specifying any special directions of group operations with respect to the original cube directions; also find the crystal system of the ordered structure and the number of types of domains which will be formed.[2]

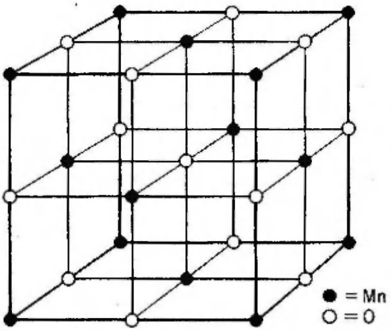

Fig. 8-18. *Cubic unit cell of* NaCl *structure.*

REFERENCES

BELOV, K. P.: "Magnetic Transitions," translated from the Russian by W. H. Furry, Consultants Bureau, New York, 1961.

BOUCKAERT, L. P., R. SMOLUCHOWSKI, and E. P. WIGNER: Theory of Brillouin Zones and Symmetry Properties of Wave Functions in Crystals, *Phys. Rev.*, **50**, 58 (1936).

HEINE, V.: "Group Theory," chap. 6, Pergamon Press, New York, 1960.

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[1] See Le Corre, *loc. cit.*

[2] See Le Corre, *loc. cit.*

AUTONOMA DE MADRID BIBLIOTECA CIENCIAS

HERRING, C.: A New Method for Calculating Wave Functions in Crystals, *Phys. Rev.*, **57**, 1169 (1940).

JONES, H.: "The Theory of Brillouin Zones and Electronic States in Crystals," North Holland Publishing Company, Amsterdam, 1960.

KITTEL, C.: "Introduction to Solid State Physics," 2d ed., John Wiley & Sons, Inc., New York, 1956.

KOSTER, G. F.: Space Groups and Their Representations, article in F. Seitz and D. Turnbull (eds.), "Solid State Physics," vol. 5, Academic Press Inc., New York, 1957.

LE CORRE, Y.: Les groupes cristallographiques magnétiques et leurs proprietés, *J. phys. radium*, **19**, 750 (1958).

PEIERLS, R. E.: "Quantum Theory of Solids," Oxford University Press, New York, 1955.

PINCHERLE, L.: Band Structure Calculations in Solids, article in A. C. Stickland (ed.), "Reports on the Progress of Physics," vol. XXIII, Physical Society, London, 1960.

REITZ, J. R.: Methods of the One-electron Theory of Solids, article in F. Seitz and D. Turnbull (eds.), "Solid State Physics," vol. 1, Academic Press Inc., New York, 1955.

SEITZ, F.: "The Modern Theory of Solids," McGraw-Hill Book Company, Inc., New York, 1940.

TAVGER, B. A., and V. M. ZAITSEV: Magnetic Symmetry of Crystals, *J. Exptl. Theoret. Phys.* (*U.S.S.R.*), **30**, 564 (1956); translation, *Soviet Phys.* (*JETP*), **3**, 430 (1956).

WILSON, A. H.: "The Theory of Metals," Cambridge University Press, New York, 1954.

ZIMAN, J. M.: "Electrons and Phonons," Oxford University Press, New York, 1960.

APPENDIX A REVIEW OF VECTORS, VECTOR SPACES, AND MATRICES

Vectors

An n-dimensional vector $\mathbf{v}$ is an ordered n-tuple of numbers, each number being a component of the vector. Two vectors are equal if all components are equal. A vector is a null vector, $\mathbf{v} = \mathbf{0}$, if and only if all components are zero. Vectors obey the rules

$$\mathbf{u} + (\mathbf{v} + \mathbf{w}) = (\mathbf{u} + \mathbf{v}) + \mathbf{w} \qquad \mathbf{u} + \mathbf{v} = \mathbf{v} + \mathbf{u}$$

$$(a + b)\mathbf{v} = a\mathbf{v} + b\mathbf{v} \qquad a(\mathbf{u} + \mathbf{v}) = a\mathbf{u} + a\mathbf{v} \qquad a(b\mathbf{v}) = ab\mathbf{v}$$

where a and b are any complex numbers. There is defined an *inner product* or *Hermitian scalar product* $(\mathbf{v}, \mathbf{w}) = \sum_k v_k^* w_k$. This product has the properties

$$(\mathbf{v}, \mathbf{w})^* = (\mathbf{w}, \mathbf{v}) \tag{A-1a}$$

$$(\mathbf{v}, \mathbf{v}) \geqq 0 \qquad 0 \text{ implies } \mathbf{v} = \mathbf{0} \tag{A-1b}$$

$$(\mathbf{v}, a\mathbf{w}) = a(\mathbf{v}, \mathbf{w}) = (a^*\mathbf{v}, \mathbf{w}) \tag{A-1c}$$

$$(\mathbf{u} + \mathbf{v}, \mathbf{w}) = (\mathbf{u}, \mathbf{w}) + (\mathbf{v}, \mathbf{w}) \tag{A-1d}$$

The length of a vector is given by $|\mathbf{v}| = [(\mathbf{v}, \mathbf{v})]^{\frac{1}{2}}$. If $|\mathbf{v}| = 1$, the vector is said to be *normalized.* We can imagine the cosine of the angle between two vectors in this space to be defined by

$$\cos \theta = \frac{|(\mathbf{v}, \mathbf{w})|}{|\mathbf{v}|\,|\mathbf{w}|}$$

This can be shown to be less than or equal to 1. If it is zero, $\mathbf{v}$ and $\mathbf{w}$ are said to be *orthogonal* vectors. A set of normalized vectors which are mutually orthogonal is often said to be *orthonormal.*

An n-dimensional *vector space* is the totality of vectors which can be formed by allowing the n-tuple components to range over all values. The particular vectors $(1, 0, 0, \ldots)$, $(0, 1, 0, 0, \ldots)$, $\ldots$, $(\ldots, 0, 0, 1)$ are called *basis vectors* for the space. Obviously any vector in the space can be written as a linear combination of these basis vectors. In other words, they are said to *span* the space. Any set of vectors such that an arbitrary vector in the space can be expressed as a linear combination of the set spans the space.

A set of m vectors is said to be *linearly independent* if $c_1\mathbf{v}_1 + c_2\mathbf{v}_2 + \cdots + c_m\mathbf{v}_m = \mathbf{0}$ implies that $c_1 = c_2 = \cdots = c_m = 0$, in other words, if no vector of the set can be expressed in terms of the others of the set alone. In an n-dimensional vector space, only n linearly independent vectors can exist.

Matrices and Transformations

A *linear transformation* of coordinates (the components of a vector position) can be expressed as

$$
\begin{aligned}
x_1' &= \alpha_{11}x_1 + \alpha_{12}x_2 + \cdots + \alpha_{1n}x_n \\
x_2' &= \alpha_{21}x_1 + \alpha_{22}x_2 + \cdots + \alpha_{2n}x_n \\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
x_n' &= \alpha_{n1}x_1 + \alpha_{n2}x_2 + \cdots + \alpha_{nn}x_n
\end{aligned}
\tag{A-2a}
$$

or more compactly as

$$x_i' = \sum_k \alpha_{ik}x_k \tag{A-2b}$$

or still more compactly as

$$\mathbf{r}' = \boldsymbol{\alpha}\mathbf{r} \tag{A-2c}$$

where r and r′ are vectors and $\boldsymbol{\alpha}$ is the transformation matrix, a square array of the coefficients α_{ik}. The standard rules for the operation of matrices on column vectors are set up so that this abbreviated vector equation is exactly equivalent to the fully written out set of equations above. Depending on the form of the matrix $\boldsymbol{\alpha}$, this transformation might induce a rotation of axes, a permutation of axes, or a reflection. For example, the xy plane can be considered to be a two-dimensional vector space, with $x = x_1$ and $y = x_2$. Then the matrix for a counterclockwise rotation of axes by 90° is $\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$. The transformation equation written out is

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} y \\ -x \end{pmatrix}$$

so that $x' = y$ and $y' = -x$, as is correct for the present example. Note that this transformation can be looked at in two ways:

1. As above, the x' are considered coordinates of the same position vector referred to a new orientation of the coordinate axes.

2. Alternatively, the x' can be considered the coordinates of a rotated position vector with respect to the original coordinate axes. In this case, the above matrix represents a rotation of the vector 90° *clockwise.* It is generally true that the sense of an operation is reversed in passing from one of these viewpoints to the other, as is geometrically evident.

Clearly two transformations are equal if and only if all n^2 coefficients in the matrices inducing the two transformations are equal.

The transformation matrix $\boldsymbol{\alpha}$ can be viewed as a *linear operator.* It is called an operator because it transforms one vector into another. It is linear because

$$\boldsymbol{\alpha}(b\mathbf{u} + c\mathbf{v}) = b\boldsymbol{\alpha}\mathbf{u} + c\boldsymbol{\alpha}\mathbf{v} \tag{A-3}$$

If we apply a second transformation by a matrix $\boldsymbol{\beta}$ after applying $\boldsymbol{\alpha}$, we have

$$x_i'' = \sum_j \beta_{ij}x_j' \qquad x_j' = \sum_k \alpha_{jk}x_k$$

or

$$x_i'' = \sum_{j,k} \beta_{ij}\alpha_{jk}x_k = \sum_k \left(\sum_j \beta_{ij}\alpha_{jk}\right)x_k = \sum_k \gamma_{ik}x_k$$

where $\boldsymbol{\gamma}$ is a single $n \times n$ matrix which accomplishes the effect of the two transformations applied in succession. In order for this to be true, $\boldsymbol{\gamma}$ must be defined by

$$\gamma_{ik} = \sum_j \beta_{ij}\alpha_{jk} \tag{A-4}$$

which is the law of *matrix multiplication.*

Matrix Properties

We now enumerate a number of the properties of matrices which we frequently utilize in the text:

1. The *determinant* of the product of two matrices is equal to the product of the determinants of the factors; i.e., if $\boldsymbol{\gamma} = \boldsymbol{\alpha\beta}$, $|\boldsymbol{\gamma}| = |\boldsymbol{\alpha}|\,|\boldsymbol{\beta}|$, where $|\boldsymbol{\alpha}|$ is the determinant of $\boldsymbol{\alpha}$.

2. Matrix multiplication need *not* be commutative; that is, $\boldsymbol{\beta\alpha}$ need not equal $\boldsymbol{\alpha\beta}$.

3. The *associative* law holds in matrix multiplication; that is, $(\boldsymbol{\alpha\beta})\boldsymbol{\gamma} = \boldsymbol{\alpha}(\boldsymbol{\beta\gamma}) = \boldsymbol{\alpha\beta\gamma}$.

4. An $n \times n$ *unit matrix* $\mathbf{E}$ exists for any n. Its elements are $E_{ik} = \delta_{ik}$. It has the property that $\mathbf{E}\boldsymbol{\alpha} = \boldsymbol{\alpha}\mathbf{E} = \boldsymbol{\alpha}$, for any $\boldsymbol{\alpha}$.

5. If $|\boldsymbol{\alpha}| \neq 0$, there is a unique *inverse* to $\boldsymbol{\alpha}$, denoted by $\boldsymbol{\alpha}^{-1}$, such that $\boldsymbol{\alpha}^{-1}\boldsymbol{\alpha} = \boldsymbol{\alpha\alpha}^{-1} = \mathbf{E}$. The inverse of a product of matrices is the product of the inverses in inverse order. The proof is obvious since $(\boldsymbol{\beta}^{-1}\boldsymbol{\alpha}^{-1})(\boldsymbol{\alpha\beta}) = \boldsymbol{\beta}^{-1}(\boldsymbol{\alpha}^{-1}\boldsymbol{\alpha})\boldsymbol{\beta} = \boldsymbol{\beta}^{-1}\boldsymbol{\beta} = \mathbf{E}$.

6. The *null matrix* has all elements equal to zero. Thus $\boldsymbol{\alpha}\mathbf{0} = \mathbf{0}\boldsymbol{\alpha} = \mathbf{0}$.

7. The *sum* of two matrices is obtained by simply adding corresponding elements. Thus, if $\boldsymbol{\gamma} = \boldsymbol{\alpha} + \boldsymbol{\beta}$, then $\gamma_{ij} = \alpha_{ij} + \beta_{ij}$. Matrix addition is thus *commutative.*

8. When a matrix is multiplied by a number, all elements are multiplied by that number. That is, if $\boldsymbol{\gamma} = c\boldsymbol{\alpha}$, then $\gamma_{ij} = c\alpha_{ij}$.

9. All *diagonal matrices* commute and have diagonal products. For example, if $D_{ik} = D_i\delta_{ik}$, and similarly for D', then $(DD')_{ij} = (D'D)_{ij} = D_iD_i'\delta_{ij}$.

10. The *trace,* or *spur,* of a matrix is the sum of its diagonal elements. That is, $\text{Tr}\ \boldsymbol{\alpha} = \sum_i \alpha_{ii}$. The trace of a product is independent of the order of the factors; for example, $\text{Tr}\ \boldsymbol{\alpha\beta} = \sum_i (\boldsymbol{\alpha\beta})_{ii} = \sum_i\sum_j \alpha_{ij}\beta_{ji} = \sum_j\sum_i \beta_{ji}\alpha_{ij} = \sum_j (\boldsymbol{\beta\alpha})_{jj} = \text{Tr}\ \boldsymbol{\beta\alpha}$.

11. A *similarity transformation* applied to a matrix $\boldsymbol{\alpha}$ yields one of the form $\boldsymbol{\beta}^{-1}\boldsymbol{\alpha\beta}$. Such transformations leave the trace invariant, since $\text{Tr}\ \boldsymbol{\beta}^{-1}(\boldsymbol{\alpha\beta}) = \text{Tr}\ (\boldsymbol{\alpha\beta})\boldsymbol{\beta}^{-1} = \text{Tr}\ \boldsymbol{\alpha}$.

12. If all matrices in a matrix equation are subjected to the same similarity transformation, the matrix equation will hold also for the transformed matrices. That is, if $\boldsymbol{\alpha}' = \mathbf{s}^{-1}\boldsymbol{\alpha}\mathbf{s}$, etc., and if $\boldsymbol{\alpha\beta} = \boldsymbol{\gamma}$, then it follows that $\boldsymbol{\alpha}'\boldsymbol{\beta}' = \boldsymbol{\gamma}'$. The importance of similarity transformations in our work stems from this property.

Generalizations

As discussed above, we have treated matrices as square arrays, in which the rows and columns have been numbered similarly $1, 2, 3, \cdots, n$. We can generalize to consider *nonsquare* matrices. The simplest case is one where the rows and columns are of equal number but are labeled differently. For example, the rows might be labeled x, y, z and the columns ξ, η, ζ. This generalization causes no difficulty with the properties described above. A further generalization is to the case of *rectangular* matrices, where the number of rows and columns is different. Matrix multiplication is still possible using the standard definition, provided that the number of columns in the first factor is equal to the number of rows in the second. That is, an $m \times n$ matrix times an $n \times p$ matrix yields an $m \times p$ product matrix. An extreme example of this is the multiplication of an $n \times n$ matrix into an $n \times 1$ column vector (matrix) to yield another $n \times 1$ column vector. Another extreme example is the multiplication of a $1 \times n$ row vector into an $n \times 1$ column vector to yield a 1×1 scalar number. Such properties as the associative law still hold, but other concepts, such as the determinant, diagonal sum, and diagonal matrices, become meaningless for rectangular matrices.

It is useful to introduce the notion of the *direct product* of two matrices denoted by $\boldsymbol{\gamma} = \boldsymbol{\alpha} \times \boldsymbol{\beta}$. The elements of the direct-product matrix have a double set of subscripts and are defined by

$$\gamma_{ij,kl} = \alpha_{ik}\beta_{jl} \tag{A-5}$$

Evidently the number of elements in the direct-product matrix is the product of the number of elements in each of the factors, and there is no restriction of equality on the number of rows and columns in the two factor matrices. It is also obvious that the direct product of two diagonal matrices is diagonal. One can readily verify that $(\boldsymbol{\alpha} \times \boldsymbol{\beta})(\boldsymbol{\alpha}' \times \boldsymbol{\beta}') = \boldsymbol{\alpha}\boldsymbol{\alpha}' \times \boldsymbol{\beta}\boldsymbol{\beta}'$, that is, that taking a direct product commutes with matrix multiplication.

Diagonalization of Matrices

Consider the *secular equation* associated with a matrix $\boldsymbol{\alpha}$, namely,

$$0 = |\boldsymbol{\alpha} - \lambda\mathbf{E}| = \begin{vmatrix} (\alpha_{11} - \lambda) & \alpha_{12} & \cdots \\ \alpha_{21} & (\alpha_{22} - \lambda) & \cdots \\ \cdots & \cdots & (\alpha_{nn} - \lambda) \end{vmatrix} \tag{A-6}$$

Now apply a similarity transformation to $\boldsymbol{\alpha}$, obtaining the matrix $\boldsymbol{\beta} = \mathbf{s}^{-1}\boldsymbol{\alpha}\mathbf{s}$, and consider the secular equation of $\boldsymbol{\beta}$. This is

$$\begin{aligned} 0 &= |\boldsymbol{\beta} - \lambda\mathbf{E}| = |\mathbf{s}^{-1}\boldsymbol{\alpha}\mathbf{s} - \lambda\mathbf{E}| = |\mathbf{s}^{-1}\boldsymbol{\alpha}\mathbf{s} - \lambda\mathbf{s}^{-1}\mathbf{E}\mathbf{s}| = |\mathbf{s}^{-1}(\boldsymbol{\alpha} - \lambda\mathbf{E})\mathbf{s}| \\ &= |\mathbf{s}^{-1}|\,|\boldsymbol{\alpha} - \lambda\mathbf{E}|\,|\mathbf{s}| = |\boldsymbol{\alpha} - \lambda\mathbf{E}|\,|\mathbf{s}^{-1}\mathbf{s}| = |\boldsymbol{\alpha} - \lambda\mathbf{E}| \end{aligned}$$

Thus *all* the roots of the secular equation, which are the *eigenvalues* λ_k of the matrix, are invariant under a similarity transformation. This is a stronger form of our previous results that the *trace*, or sum of eigenvalues, and the *determinant*, or product of eigenvalues, are invariant.

The significance of an eigenvalue λ_k of the matrix $\boldsymbol{\alpha}$ is that for these values there are nontrivial solutions to the matrix equation

$$\boldsymbol{\alpha}\mathbf{v}^k = \lambda_k\mathbf{v}^k \tag{A-7}$$

The *eigenvectors* $\mathbf{v}^k$ are defined by this equation. They have the property of being unchanged in direction by the operation of the transformation $\boldsymbol{\alpha}$. That is, they define the *principal axes* of the system. The eigenvalues λ_k give the degree of "stretching" of the vector $\mathbf{v}^k$ produced by $\boldsymbol{\alpha}$.

Collecting the n eigenvectors (for an $n \times n$ matrix), we can form a matrix $\mathbf{V}$ of the form

$$\mathbf{V} = (\mathbf{v}^1\mathbf{v}^2 \cdots \mathbf{v}^n) \tag{A-8a}$$

in which

$$V_{ik} = (v^k)_i \tag{A-8b}$$

If we also form a diagonal matrix of the eigenvalues

$$\Lambda_{ik} = \Lambda_{ki} = \lambda_k\delta_{ik} \tag{A-9}$$

we can write a typical example of the eigenvalue equation (A-7) as

$$\sum_j \alpha_{ij}(v^k)_j = \sum_j \alpha_{ij}V_{jk} = \lambda_k(v^k)_i = \lambda_k V_{ik} = \sum_j \lambda_k\delta_{jk}V_{ij} = \sum_j V_{ij}\Lambda_{jk}$$

or

$$\boldsymbol{\alpha}\mathbf{V} = \mathbf{V}\boldsymbol{\Lambda}$$

or

$$\mathbf{V}^{-1}\boldsymbol{\alpha}\mathbf{V} = \boldsymbol{\Lambda} \tag{A-10}$$

Thus we have shown that the (unitary) transformation matrix $\mathbf{V}$ composed of the (normalized) column eigenvectors of $\boldsymbol{\alpha}$ provides a similarity transformation which diagonalizes $\boldsymbol{\alpha}$, leaving the eigenvalues on the diagonal. In this form, it is clear that the eigenvalues λ_k do, in fact, form the solutions of the secular equation (A-6).

Nomenclature and Properties of Special Matrices

The *transpose* of a matrix $\boldsymbol{\alpha}$, denoted by $\tilde{\boldsymbol{\alpha}}$, is obtained from $\boldsymbol{\alpha}$ by reflecting across the principal diagonal, so that $\tilde{\alpha}_{ij} = \alpha_{ji}$. Evidently then, $(\widetilde{\boldsymbol{\alpha\beta}}) = \tilde{\boldsymbol{\beta}}\tilde{\boldsymbol{\alpha}}$.

The *complex conjugate* of a matrix $\boldsymbol{\alpha}$, denoted by $\boldsymbol{\alpha}^*$, is obtained by taking the complex conjugate of all matrix elements, so that $(\alpha^*)_{ij} = (\alpha_{ij})^*$. Evidently, this leaves products in the same order.

The *adjoint* of a matrix $\boldsymbol{\alpha}$, denoted by $\boldsymbol{\alpha}^\dagger$, is the transpose of the complex conjugate. That is, $\boldsymbol{\alpha}^\dagger = \tilde{\boldsymbol{\alpha}}^*$, and $(\alpha^\dagger)_{ij} = \alpha^*_{ji}$. The product rule is then $(\boldsymbol{\alpha\beta})^\dagger = \boldsymbol{\beta}^\dagger\boldsymbol{\alpha}^\dagger$.

A *Hermitian*, or *self-adjoint*, matrix H has the property that $\mathbf{H}^\dagger = \mathbf{H}$, or that $H_{ij} = H^*_{ji}$.

A *unitary* matrix is one whose inverse is the adjoint. That is, $\mathbf{U}^\dagger = \mathbf{U}^{-1}$, so that $(U^{-1})_{ij} = U^*_{ji}$.

A *real orthogonal* matrix can be viewed as a unitary matrix, with the restriction that all elements are real. Thus $\mathbf{R}^{-1} = \mathbf{R}^\dagger = \tilde{\mathbf{R}}$, and $(R^{-1})_{ij} = R_{ji}$. Transformations between orthogonal coordinate systems are carried out by such matrices.

Some properties of these special types of matrices are as follows:

1. The Hermitian scalar product is unchanged if the adjoint of a given operator is transferred to the other factor in the product. For example,

$$(\mathbf{v}, \boldsymbol{\alpha}\mathbf{w}) = (\boldsymbol{\alpha}^\dagger\mathbf{v}, \mathbf{w})$$

2. The rows (or columns) of any unitary matrix form a set of n orthonormal vectors.

3. A unitary transformation applied to both vectors leaves the Hermitian scalar product unchanged. That is,

$$(\mathbf{Uv}, \mathbf{Uw}) = (\mathbf{v}, \mathbf{U}^{\dagger}\mathbf{Uw}) = (\mathbf{v}, \mathbf{U}^{-1}\mathbf{Uw}) = (\mathbf{v}, \mathbf{w})$$

4. The product of two unitary matrices is unitary, since $(\mathbf{UV})^{\dagger} = \mathbf{V}^{\dagger}\mathbf{U}^{\dagger} = \mathbf{V}^{-1}\mathbf{U}^{-1} = (\mathbf{UV})^{-1}$.

5. Both unitary and Hermitian matrices can always be diagonalized by similarity transformations using unitary matrices as indicated above. (Singular matrices with determinant zero could not be, for example.) The eigenvalues of Hermitian matrices are real. The eigenvalues of unitary matrices are of absolute value unity; if $\mathbf{U}$ is actually real orthogonal, the eigenvalues appear in complex-conjugate pairs.

REFERENCES

HILDEBRAND, F. B.: "Methods of Applied Mathematics," chap. 1, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1952.

MARGENAU, H., and G. M. MURPHY: "The Mathematics of Physics and Chemistry," chap. 10, D. Van Nostrand Company, Inc., Princeton, N. J., 1943.

WIGNER, E. P.: "Group Theory," chaps. 1–3, Academic Press Inc., New York, 1959.

APPENDIX B CHARACTER TABLES FOR POINT-SYMMETRY GROUPS

In this Appendix we give the character tables for the 32 crystallographic point groups, together with 5 point groups involving fivefold rotations and 2 point groups involving C_∞. These 7 additional groups are not possible in crystals, but they may occur in molecules. When a group is conveniently given as the direct product of a smaller group and the group of the inversion i, this fact is indicated rather than giving the table, since the desired table can be obtained easily from that of the smaller group by use of the method indicated in Sec. 3-9.

Each table is labeled with the group designation in the Schoenflies notation, as developed in the text. To assist in making contact with other references, we also parenthetically quote the group designation in the shortened international notation used in the International Tables for X-ray Crystallography. In this notation, a number n refers to an n-fold rotation axis, i.e., rotation by $2\pi/n$. The notation n refers to rotoinversion, obtained by combining an n-fold rotation with the inversion. Thus $\bar{1}$ is just the inversion itself, and 2 is a reflection in the plane perpendicular to the rotation axis. A reflection is usually denoted m, for mirror plane. When the reflection is in the "horizontal" plane, the m is placed in the "denominator" of the symbol, which in the shortened notation is $/m$. For further details on this notation, the reader is referred to the literature.

The irreducible representations are labeled as discussed in the text. Briefly, A and B always refer to one-dimensional representations, E refers to two-dimensional representations, and T refers to three-dimensional representations. Pairs of complex-conjugate representations are bracketed together and labeled as a two-dimensional representation E, because time-reversal symmetry makes them degenerate. The subscripts g and u, for gerade and ungerade, indicate even and odd representations under inversion. In addition to these representation labels, we also indicate the transformation properties of the coordinates x, y, z, of various bilinear combinations of coordinates, and of the infinitesimal rotations R_x, R_y, and R_z.

C_1 (1)	E
A	1

C_2 (2)			E	C_2
x^2, y^2, z^2, xy	R_z, z	A	1	1
xz, yz	x, y R_x, R_y	B	1	-1

C_3 (3)			E	C_3	C_3^2
$x^2 + y^2, z^2$	R_z, z	A	1	1	1
(xz, yz) $(x^2 - y^2, xy)$	(x, y) (R_x, R_y)	E	1	ω	ω^2
			1	ω^2	ω

$\omega = e^{2\pi i/3}$

C_4 (4)			E	C_2	C_4	C_4^3
$x^2 + y^2, z^2$	R_z, z	A	1	1	1	1
$x^2 - y^2, xy$		B	1	1	-1	-1
(xz, yz)	(x, y) (R_x, R_y)	E	1	-1	i	$-i$
			1	-1	$-i$	i

C_5 (5)			E	C_5	C_5^2	C_5^3	C_5^4
$x^2 + y^2, z^2$	R_z, z	A	1	1	1	1	1
(xz, yz)	(x, y) (R_x, R_y)	E'	1	ω	ω^2	ω^3	ω^4
			1	ω^4	ω^3	ω^2	ω
$(x^2 - y^2, xy)$		E''	1	ω^2	ω^4	ω	ω^3
			1	ω^3	ω	ω^4	ω^2

$\omega = e^{2\pi i/5}$

C_6 (6)			E	C_6	C_3	C_2	C_3^2	C_6^5
$x^2 + y^2, z^2$	R_z, z	A	1	1	1	1	1	1
		B	1	-1	1	-1	1	-1
(xz, yz)	(x, y) (R_x, R_y)	E'	1	ω	ω^2	ω^3	ω^4	ω^5
			1	ω^5	ω^4	ω^3	ω^2	ω
$(x^2 - y^2, xy)$		E''	1	ω^2	ω^4	1	ω^2	ω^4
			1	ω^4	ω^2	1	ω^4	ω^2

$\omega = e^{2\pi i/6}$

C_{2v} (2*mm*)			E	C_2	σ_v	σ_v'
x^2, y^2, z^2	z	A_1	1	1	1	1
xy	R_z	A_2	1	1	-1	-1
xz	R_y, x	B_1	1	-1	1	-1
yz	R_x, y	B_2	1	-1	-1	1

C_{3v} (3*m*)			E	$2C_3$	$3\sigma_v$
$x^2 + y^2, z^2$	z	A_1	1	1	1
	R_z	A_2	1	1	-1
$(x^2 - y^2, xy)$ (xz, yz)	(x, y) (R_x, R_y)	E	2	-1	0

C_{4v} (4*mm*)			E	C_2	$2C_4$	$2\sigma_v$	$2\sigma_d$
$x^2 + y^2, z^2$	z	A_1	1	1	1	1	1
	R_z	A_2	1	1	1	-1	-1
$x^2 - y^2$		B_1	1	1	-1	1	-1
xy		B_2	1	1	-1	-1	1
(xz, yz)	(x, y) (R_x, R_y)	E	2	-2	0	0	0

C_{5v} (5*m*)			E	$2C_5$	$2C_5^2$	$5\sigma_v$
$x^2 + y^2, z^2$	z	A_1	1	1	1	1
	R_z	A_2	1	1	1	-1
(xz, yz)	(x, y) (R_x, R_y)	E_1	2	$2\cos x$	$2\cos 2x$	0
$(x^2 - y^2, xy)$		E_2	2	$2\cos 2x$	$2\cos 4x$	0

$x = \dfrac{2\pi}{5}$

C_{6v} (6*mm*)			E	C_2	$2C_3$	$2C_6$	$3\sigma_d$	$3\sigma_v$
$x^2 + y^2, z^2$	z	A_1	1	1	1	1	1	1
	R_z	A_2	1	1	1	1	-1	-1
		B_1	1	-1	1	-1	-1	1
		B_2	1	-1	1	-1	1	-1
(xz, yz)	(x, y) (R_x, R_y)	E_1	2	-2	-1	1	0	0
$(x^2 - y^2, xy)$		E_2	2	2	-1	-1	0	0

$C_{1h}\ (m)$			E	σ_h
x^2, y^2, z^2, xy	R_z, x, y	A'	1	1
xz, yz	R_x, R_y, z	A''	1	−1

$C_{2h}\ (2/m)$			E	C_2	σ_h	i
x^2, y^2, z^2, xy	R_z	A_g	1	1	1	1
	z	A_u	1	1	−1	−1
xz, yz	R_x, R_y	B_g	1	−1	−1	1
	x, y	B_u	1	−1	1	−1

$C_{3h} - C_3 \times \sigma_h\ (\bar{6})$			E	C_3	C_3^2	σ_h	S_3	$(\sigma_h C_3^2)$
$x^2 + y^2, z^2$	R_z	A'	1	1	1	1	1	1
	z	A''	1	1	1	−1	−1	−1
$(x^2 - y^2, xy)$	(x, y)	E'	1	ω	ω^2	1	ω	ω^2
			1	ω^2	ω	1	ω^2	ω
(xz, yz)	(R_x, R_y)	E''	1	ω	ω^2	−1	$-\omega$	$-\omega^2$
			1	ω^2	ω	−1	$-\omega^2$	$-\omega$

$\omega = e^{2\pi i/3}$

$C_{4h} = C_4 \times i \qquad (4/m)$

$C_{5h} = C_5 \times \sigma_h \qquad (\overline{10})$

$C_{6h} = C_6 \times i \qquad (6/m)$

$S_2\ (\bar{1})$			E	i
$x^2, y^2, z^2, xy, xz, yz$	R_x, R_y, R_z	A_g	1	1
	x, y, z	A_u	1	−1

$S_4\ (\bar{4})$			E	C_2	S_4	S_4^3
$x^2 + y^2, z^2$	R_z	A	1	1	1	1
	z	B	1	1	−1	−1
(xz, yz) $(x^2 - y^2, xy)$	(x, y) (R_x, R_y)	E	1	−1	i	$-i$
			1	−1	$-i$	i

$S_6 = C_3 \times i \qquad (\bar{3})$

D_2 (222)			E	C_2^z	C_2^y	C_2^x
x^2, y^2, z^2		A_1	1	1	1	1
xy	R_z, z	B_1	1	1	−1	−1
xz	R_y, y	B_2	1	−1	1	−1
yz	R_x, x	B_3	1	−1	−1	1

D_3 (32)			E	$2C_3$	$3C_2'$
$x^2 + y^2, z^2$		A_1	1	1	1
	R_z, z	A_2	1	1	−1
(xz, yz) $(x^2 - y^2, xy)$	(x, y) (R_x, R_y)	E	2	−1	0

D_4 (422)			E	$C_2 - C_4^2$	$2C_4$	$2C_2'$	$2C_2''$
$x^2 + y^2, z^2$		A_1	1	1	1	1	1
	R_z, z	A_2	1	1	1	−1	−1
$x^2 - y^2$		B_1	1	1	−1	1	−1
xy		B_2	1	1	−1	−1	1
(xz, yz)	(x, y) (R_x, R_y)	E	2	−2	0	0	0

D_5 (52)			E	$2C_5$	$2C_5^2$	$5C_2'$
$x^2 + y^2, z^2$		A_1	1	1	1	1
	R_z, z	A_2	1	1	1	−1
(xz, yz)	(x, y) (R_x, R_y)	E_1	2	$2 \cos x$	$2 \cos 2x$	0
$(x^2 - y^2, xy)$		E_2	2	$2 \cos 2x$	$2 \cos 4x$	0

$x = \frac{2\pi}{5}$

D_6 (622)			E	C_2	$2C_3$	$2C_6$	$3C_2'$	$3C_2''$
$x^2 + y^2, z^2$		A_1	1	1	1	1	1	1
	R_z, z	A_2	1	1	1	1	−1	−1
		B_1	1	−1	1	−1	1	−1
		B_2	1	−1	1	−1	−1	1
(xz, yz)	(x, y) (R_x, R_y)	E_1	2	−2	−1	1	0	0
$(x^2 - y^2, xy)$		E_2	2	2	−1	−1	0	0

D_{2d} $(42m)$			E	C_2	$2S_4$	$2C_2'$	$2\sigma_d$
$x^2 + y^2, z^2$		A_1	1	1	1	1	1
	R_z	A_2	1	1	1	−1	−1
$x^2 - y^2$		B_1	1	1	−1	1	−1
xy	z	B_2	1	1	−1	−1	1
(xz, yz)	(x, y) (R_x, R_y)	E	2	−2	0	0	0

$$D_{3d} = D_3 \times i \qquad (\bar{3}m)$$

$$D_{2h} = D_2 \times i \qquad (mmm)$$

$D_{3h} = D_3 \times \sigma_h$ $(6m2)$			E	σ_h	$2C_3$	$2S_3$	$3C_2'$	$3\sigma_v$
$x^2 + y^2, z^2$		A_1'	1	1	1	1	1	1
	R_z	A_2'	1	1	1	1	−1	−1
		A_1''	1	−1	1	−1	1	−1
	z	A_2''	1	−1	1	−1	−1	1
$(x^2 - y^2, xy)$	(x, y)	E'	2	2	−1	−1	0	0
(xz, yz)	(R_x, R_y)	E''	2	−2	−1	1	0	0

$$D_{4h} = D_4 \times i \qquad (4/mmm)$$

$$D_{5h} = D_5 \times \sigma_h \qquad (\overline{10}m2)$$

$$D_{6h} = D_6 \times i \qquad (6/mmm)$$

T (23)		E	$3C_2$	$4C_3$	$4C_3'$
	A	1	1	1	1
	E	1	1	ω	ω^2
		1	1	ω^2	ω
(R_x, R_y, R_z) (x, y, z)	T	3	−1	0	0

$\omega = e^{2\pi i/3}$

$$T_h = T \times i \qquad (m3)$$

$O\ (432)$		E	$8C_3$	$3C_2 = 3C_4^2$	$6C_2$	$6C_4$
	A_1	1	1	1	1	1
	A_2	1	1	1	−1	−1
$(x^2 - y^2, 3z^2 - r^2)$	E	2	−1	2	0	0
(R_x, R_y, R_z) (x, y, z)	T_1	3	0	−1	−1	1
(xy, yz, zx)	T_2	3	0	−1	1	−1

$O_h = O \times i \qquad (m3m)$

$T_d\ (\bar{4}3m)$		E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
	A_1	1	1	1	1	1
	A_2	1	1	1	−1	−1
	E	2	−1	2	0	0
(R_x, R_y, R_z)	T_1	3	0	−1	−1	1
(x, y, z)	T_2	3	0	−1	1	−1

$C_{\infty v}\ (\infty m)$			E	$2C_\phi$	σ_v
$x^2 + y^2, z^2$	z	$A_1(\Sigma^+)$	1	1	1
	R_z	$A_2(\Sigma^-)$	1	1	−1
(xz, yz)	(x, y) (R_x, R_y)	$E_1(\Pi)$	2	$2\cos\phi$	0
$(x^2 - y^2, xy)$		$E_2(\Delta)$	2	$2\cos 2\phi$	0
		· · ·	· · ·	· · ·	· · ·

$D_{\infty h}\ (\infty/mm)$			E	$2C_\phi$	C_2'	i	$2iC_\phi$	iC_2'
$x^2 + y^2, z^2$		$A_{1g}(\Sigma_g^+)$	1	1	1	1	1	1
		$A_{1u}(\Sigma_u^+)$	1	1	1	−1	−1	−1
	R_z	$A_{2g}(\Sigma_g^-)$	1	1	−1	1	1	−1
	z	$A_{2u}(\Sigma_u^-)$	1	1	−1	−1	−1	1
(xz, yz)	(R_x, R_y)	$E_{1g}(\Pi_g)$	2	$2\cos\phi$	0	2	$2\cos\phi$	0
	(x, y)	$E_{1u}(\Pi_u)$	2	$2\cos\phi$	0	−2	$-2\cos\phi$	0
$(x^2 - y^2, xy)$		$E_{2g}(\Delta_g)$	2	$2\cos 2\phi$	0	2	$2\cos 2\phi$	0
		$E_{2u}(\Delta_u)$	2	$2\cos 2\phi$	0	−2	$-2\cos 2\phi$	0
		· · ·	· · ·	· · ·	· · ·	· · ·	· · ·	· · ·

REFERENCES

EYRING, H., J. WALTER, and G. E. KIMBALL: "Quantum Chemistry," app. VII, John Wiley & Sons, Inc., New York, 1944.

HEINE, V.: "Group Theory," chap. III and apps. J, K, and L, Pergamon Press, New York, 1960.

"International Tables for X-ray Crystallography," Kynoch Press, Birmingham, 1952.

ROSENTHAL, J. E., and G. M. MURPHY: Group Theory and the Vibrations of Polyatomic Molecules, *Revs. Modern Phys.*, **8**, 317 (1936).

APPENDIX C TABLE OF c^k AND a^k COEFFICIENTS FOR s, p, AND d ELECTRONS

These coefficients are defined in Eqs. (6-37) and (6-40), respectively, of the text. Note that $c^k(lm, l'm') = (-1)^{m-m'}c^k(l'm', lm)$, whereas $a^k(lm, l'm')$ is unchanged under an interchange of arguments. The values of l and l' are indicated by the usual spectroscopic notations s, p, d.

Table C-1

Table of coefficients $c^k(lm, l'm')$

	m	m'	$k = 0$
ss	0	0	1

	m	m'	$k = 1$
sp	0	± 1	$-\sqrt{\frac{1}{3}}$
	0	0	$\sqrt{\frac{1}{3}}$

	m	m'	$k = 2$
sd	0	± 2	$\sqrt{\frac{1}{5}}$
	0	± 1	$-\sqrt{\frac{1}{5}}$
	0	0	$\sqrt{\frac{1}{5}}$

	m	m'	$k = 0$	$k = 2$
pp	± 1	± 1	1	$-\sqrt{\frac{1}{25}}$
	± 1	0	0	$\sqrt{\frac{3}{25}}$
	± 1	∓ 1	0	$-\sqrt{\frac{6}{25}}$
	0	0	1	$\sqrt{\frac{4}{25}}$

Table C-1—*continued*

	m	m'	$k = 1$	$k = 3$	
pd	±1	±2	$-\sqrt{\frac{6}{15}}$	$\sqrt{\frac{3}{245}}$	
	±1	±1	$\sqrt{\frac{3}{15}}$	$-\sqrt{\frac{9}{245}}$	
	±1	0	$-\sqrt{\frac{1}{15}}$	$\sqrt{\frac{18}{245}}$	
	±1	∓1	0	$-\sqrt{\frac{30}{245}}$	
	±1	∓2	0	$\sqrt{\frac{45}{245}}$	
	0	±2	0	$\sqrt{\frac{15}{245}}$	
	0	±1	$-\sqrt{\frac{3}{15}}$	$-\sqrt{\frac{24}{245}}$	
	0	0	$\sqrt{\frac{4}{15}}$	$\sqrt{\frac{27}{245}}$	
	m	m'	$k = 0$	$k = 2$	$k = 4$
dd	±2	±2	1	$-\sqrt{\frac{4}{49}}$	$\sqrt{\frac{1}{441}}$
	±2	±1	0	$\sqrt{\frac{6}{49}}$	$-\sqrt{\frac{5}{441}}$
	±2	0	0	$-\sqrt{\frac{4}{49}}$	$\sqrt{\frac{15}{441}}$
	±2	∓1	0	0	$-\sqrt{\frac{35}{441}}$
	±2	∓2	0	0	$\sqrt{\frac{70}{441}}$
	±1	±1	1	$\sqrt{\frac{1}{49}}$	$-\sqrt{\frac{16}{441}}$
	±1	0	0	$\sqrt{\frac{1}{49}}$	$\sqrt{\frac{30}{441}}$
	±1	∓1	0	$-\sqrt{\frac{6}{49}}$	$-\sqrt{\frac{40}{441}}$
	0	0	1	$\sqrt{\frac{4}{49}}$	$\sqrt{\frac{36}{441}}$

Table C-2

Table of coefficients $a^k(lm, l'm')$

	m	m'	$k = 0$	$k = 2$	$k = 4$
ss	0	0	1	0	0
sp	0	±1	1	0	0
	0	0	1	0	0
sd	0	±2	1	0	0
	0	±1	1	0	0
	0	0	1	0	0
pp	±1	±1	1	$\frac{1}{25}$	0
	±1	0	1	$-\frac{2}{25}$	0
	0	0	1	$\frac{4}{25}$	0
pd	±1	±2	1	$\frac{2}{35}$	0
	±1	±1	1	$-\frac{1}{35}$	0
	±1	0	1	$-\frac{2}{35}$	0
	0	±2	1	$-\frac{4}{35}$	0
	0	±1	1	$\frac{2}{35}$	0
	0	0	1	$\frac{4}{35}$	0
dd	±2	±2	1	$\frac{4}{49}$	$\frac{1}{441}$
	±2	±1	1	$-\frac{2}{49}$	$-\frac{4}{441}$
	±2	0	1	$-\frac{4}{49}$	$\frac{6}{441}$
	±1	±1	1	$\frac{1}{49}$	$\frac{16}{441}$
	±1	0	1	$\frac{2}{49}$	$-\frac{24}{441}$
	0	0	1	$\frac{4}{49}$	$\frac{36}{441}$

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